

ZDOC/9404

ZERO DISCHARGE ORGANIC COATINGS

Powder Paint - UV Curable Paint - E-Coat

Quarterly Technical Report
October 1994 - December 1994

Prepared By: Dr. James Leal - Hughes Missile Systems Company
Stephen J. Spadafora - Naval Air Warfare Center- Aircraft Division, Warminster, Pa.
Dr. Richard D. Granata - Lehigh University
Steven R. Felstein - Hughes Aircraft Company
Dr. Srin Raghavan - University of Arizona

Hughes Missile Systems Company
P.O. Box 11337
Tucson, AZ 85734



Sponsored by
Advanced Research Projects Agency
Defense Sciences Office
Environmental Technology Research and Development Initiative
ARPA Order No. 9328/06
Issued by ARPA/CMO under Contract #MDA972-93-C-0020

The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Advanced Research Projects Agency or the U.S. Government.

19950314 089

DTIC QUALITY INSPECTED 5

Approved for public release; distribution is unlimited.

ZERO DISCHARGE ORGANIC COATINGS

Powder Paint - UV Curable Paint - E-Coat

Quarterly Report
October 1994 - December 1994

Abstract

The Zero Discharge Organic Coatings (ZDOC) R&D project will substantially advance coatings technology through the development of high performance zero-discharge coating systems. Development efforts are proceeding on three coating technologies, powder paint, Ultraviolet (UV) curable paint and electro-coating (E-coat) paint. These three paint technologies offer the potential of high performance coatings with no volatile organic compound (VOC) emissions or hazardous waste generation. These three technologies and their associated application processes will be applicable to a wide variety of military equipment and structures, thereby eliminating volatile organic compound (VOC's) and toxic heavy metals from coatings and painting operations.

The ZDOC team of Hughes Aircraft Company, Lehigh University, University of Arizona, and the Naval Air Warfare Center Aircraft Division Warminster offers a blend of experience, expertise, and capabilities in all aspects of organic coatings technology. This quarterly report reviews the team's technical activities and results during the period October 1994 - December 1994.

Accession For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
Unannounced <input type="checkbox"/>	
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Approved for public release; distribution is unlimited.

ZERO DISCHARGE ORGANIC COATINGS

Powder Paint - UV Curable Paint - E-Coat

Contents

Abstract	ii
List of Acronyms and Abbreviations.	iv
Summary	1
Introduction.	1
Technical Problems	2
General Methodology	5
Technical Results	7
Important Findings and Conclusions	12
Significant Hardware Developments	13
Special Comments	13
Implications for Further Research	13
References	13
Appendixes	14
Appendix A: UV Curing of Powders - Test Results.	15
Appendix B: Powder Coating of Non-conductive Substrates	23
Appendix C: IR Cure Profile Results	38
Appendix D: Powder Coating Development Test Results	41

ZERO DISCHARGE ORGANIC COATINGS

Powder Paint - UV Curable Paint - E-Coat

Quarterly Report
October 1994 - December 1994

List of Acronyms and Abbreviations

CRADA	Cooperative Research and Development Agreement
E-Coat	Electrocoat
HAC	Hughes Aircraft Company
HMSC	Hughes Missile Systems Company
IR	Infra Red
NAWCADWAR	Naval Air Warfare Center - Aircraft Division - Warminster, Pa
UofA	University of Arizona
UV	Ultraviolet
ZDOC	Zero Discharge Organic Coatings
TPE	Total Performance Evaluation

Approved for public release; distribution is unlimited.

ZERO DISCHARGE ORGANIC COATINGS

Powder Paint - UV Curable Paint - E-Coat

SUMMARY

This report summarizes the research efforts of the ZDOC project team during the three month period from October 1994 through December 1994. The ZDOC project team is comprised of 5 teams from different organizations (HMSC, NAWCADWAR, HAC-TSD, Lehigh & UofA) each working in separate but related portions of the overall ZDOC project. The baseline technical, administrative, personnel and facility tasks required to begin the advanced coating development program are largely completed and advanced coating formulation activities are being initiated. Team activities and accomplishments during this quarter include:

- Completed testing of first iteration inhibited powder coatings.
- IR oven profiled and preliminary cure testing of powder coatings started.
- Continued characterization of conductive agents for powder coating non-conductive substrates. Prepared publication on coating non-conductive substrates.
- Positron studies used to identify free volume of cured resins.
- Sample model designed and resin system selected for identifying mechanism of corrosion inhibitors.
- Evaluation of E-coat and powder materials via EIS and other techniques continued.
- Continued evaluating methods for determining the quality of conversion coated substrates.
- Continued developing operating procedures and methods for electrocoat process line.

1.0 INTRODUCTION

Organic coatings, which provide the primary defense against environmental degradation of military equipment, have been identified as a major source of hazardous material emissions and waste in the Department of Defense. The current approach to solving this problem is through the incremental reduction of the coatings' toxic components. In contrast, the Zero Discharge Organic Coatings (ZDOC) R&D project will substantially advance coatings technology through the development of high performance zero-discharge coating systems. Development efforts are proceeding on three coating technologies: powder paint, ultraviolet (UV) curable paint and electro-coating paint. These three paint technologies offer the potential of high performance coatings with no volatile organic compound (VOC) emissions or hazardous waste generation. These three technologies and their associated application processes will be applicable to a wide variety of military equipment and structures, thereby eliminating volatile organic compound (VOC's) and toxic heavy metals from coatings and painting operations.

The ZDOC team of Hughes Aircraft Company, Lehigh University, University of Arizona, and the Naval Air Warfare Center Aircraft Division Warminster offers a blend of experience, expertise, and capabilities in all aspects of organic coatings technology. The ZDOC project involves research and development in several related coating development and application areas including advanced powder, UV curable and E-coat paint development. Table 1 summarizes the major tasks and team members involved in the ZDOC project.

Table 1. Zero Discharge Organic Coatings Project Team Assignments

Task	Organizations
Material Development Tasks	
Corrosion Inhibitor Materials	NAWCADWAR , Lehigh
Powder Paint	HMSC , NAWCADWAR, Lehigh, HAC
UV Cure Paint	HAC , NAWCADWAR, Lehigh
E-Coat Paint	Lehigh , NAWCADWAR
Applications Development Tasks	
Powder Paint - IR Cure	HMSC , UofA
Powder Painting Non-conductive materials	HMSC , UofA
UV-Cure Applications Techniques	HAC
Project Management	HMSC

Note: Primary team organization for each task is listed in **BOLD**.

The task objectives for the period of October 1994 through December 1994 were as follows:

Hughes TSD: Continued development of photocurable resins suitable for use with non-toxic corrosion inhibiting pigments.

Lehigh University: Complete development of model to evaluate mechanism of corrosion inhibitors. Identify free volume of cured resin using positron methods and support NAWC in evaluating quality of conversion coatings.

HMSC Tucson: Complete painting and testing of first iteration inhibited powder coatings. Profile IR oven for cure schedule and evaluate cure properties of coatings.

NAWC: Complete testing of first iteration inhibited powder coatings and continue evaluating methods to determine quality of conversion coated substrates.

Lehigh/NAWC: Continue developing proper operational methods for Electrocoat process line and continue EIS testing and data analysis.

University of Arizona: Prepare technical paper for The Metallurgical Society Annual Meeting on powder coating non-conductive substrates. Continue evaluation of mechanisms of surface conductivity enhancing materials.

2.0 TECHNICAL PROBLEMS

2.1 Photocurable Coatings

2.1.1 Material Supplier Selection Criteria. The requirements of this program have been extremely difficult for suppliers to meet. The vendors contacted were informed the products they submit must have the following characteristics:

- UV Curable, both clear and pigmented
- Zero Discharge, Zero VOC
- Shadow curable
- Sprayable

These characteristics are extremely challenging and many candidates failed screening tests. Due to this difficulty, it was decided the above requirements be goals for the vendors to meet rather than prerequisites for participation. In spite of the loosening of the requirements for material submittals, many of the paint suppliers supplying to military paint specifications declined to participate due to marketing reasons. Suppliers did not believe the demand for this material would warrant the R&D needed for formulation development. It was therefore necessary to issue contracts to two organizations, Sokol Enterprises and the Navy Surface Warfare Center (NSWC) to insure their participation.

2.1.2 Performance Property Testing. The properties most difficult to pass have been dry and wet tape adhesion to aluminum, impact flexibility, heat resistance and solvent resistance. One supplier, Sokol Enterprises, supplied eight different formulations before submitting one that met all requirements.

2.1.3 Pigmentation of Clearcoats. This contract requires the inclusion of NAWC's nonchromated corrosion inhibiting pigments and a hiding pigment. Pigmentation can interfere with the penetration of the UV energy needed for curing. Preliminary screening tests with low concentrations of each pigment separately and one mixture showed very strong absorption across the 250 to 450 nanometers range for most of the nonchromated corrosion resistant pigments. Table I showing the absorption/transmission data obtained is included in Appendix A.

2.2 *Inhibitor Modeling and Characterization*

2.2.1 Chromate Conversion Coating Evaluations. Difficulties in obtaining good quality test coupons led to an effort to develop a method to analyze the quality of chromate conversion coating pretreatments on aluminum. Currently, the only disclosed evaluation procedure available is that specified in military specifications MIL-C-81706 and MIL-C-5541. These specifications require testing the adhesion of a standard paint over the conversion coating in question and subjecting the bare conversion coating to one or two weeks of salt fog exposure. Several deficiencies are evident in this procedure, including the duration of the tests and the inability to non-destructively test actual components.

2.2.2 Non-Toxic Corrosion Inhibiting Pigments. NAWC has provided non-toxic, corrosion inhibiting pigment packages for incorporation into the three coating technologies under investigation for the ZDOC program. We are currently working with the other ZDOC members and the commercial companies to determine the proper inhibitor loading levels for each resin technology.

2.2.3 Electrochemical Impedance Spectroscopy Testing. EIS testing is continuing on both E'coat and powder coat samples available at NAWC. Several sample materials have reached 6000 hours of EIS testing in 3.5 % NaCl. They are still exhibiting the capacitive behavior as reported for the previous quarter. These tests do not provide an accelerated measure of coating degradation or substrate corrosion nor do they distinguish between different coating systems. Accordingly, we are investigating additional EIS methods which can provide information more rapidly.

This quarter a significant portion of the EIS work involved analyzing the impedance spectra after exposure of E'coat materials to the SO₂ salt fog for various durations. A uniform batch of scribed, E'coated aluminum panels obtained from Mac-Air was used for this latest study. The SO₂ salt fog exposure accelerates the degradation of the coating. EIS measurements performed on the unscribed portion of the panel indicate that the coating is breaking down even though no visual degradation is evident.

To properly analyze impedance spectra one must establish that the system meets the test of stationarity. This means that the impedance spectra does not change during the course of the measurement. Many of the samples exhibit stationarity but several samples were found that did not exhibit stationarity. It appears that good stationarity is associated with the extent of degradation as measured by the coating resistance. In any event, future work will require attention to this factor.

2.3 Powder Coating Non-conductive Substrates

Much of the work to date has involved characterization of the antistats being used to render the surface of non-conductive substrates conductive. In addition, the ability to powder paint specific non-conductive substrates treated with the antistat has been investigated. During morphology and microstructure analysis of the coatings formed it was noted that voids were forming in the coating although they were not present on the surface of the coating. These voids have not effected the physical performance of the coating. Testing performed to date illustrate the voids are being caused by the polymeric substrate and the antistat, but the antistat does not cause the voids to the extent caused by the polymeric substrate. More characterization of the voids will be performed.

2.4 IR Curing of Powder Coatings

The cure profile using the IR oven purchased under this program is slightly different than the cure schedule identified by the paint supplier. A longer peak temperature is required that requires the part to be stopped within the oven to reach the required peak temperature and time to receive full cure. This is not an issue for this development task but will be monitored for its impact on potential implementation.

2.5 Powder Coating Development

The development of powder coatings has involved the development and testing of both inhibited and non-inhibited powder coatings. NAWC has performed testing on substrates coated by the supplier. HMSC has performed the powder coating of the test substrates as well as the testing on the same coating formulations being tested at NAWC. The results were compared and differences have been identified.

2.6 Electrocoatings Development

2.6.1 Establish an Electrocoat Process Line. The development of corrosion inhibitor containing E'coat materials requires the establishment of an on site process line. Panels produced in this line must be sufficiently free of film defects to allow for proper testing. Producing panels of sufficient quality requires the development of the proper techniques in both producing the bath and operating each stage of the process. All four stages of the line, which includes metal pretreatment, electrodeposition bath, rinse and coating cure, must operate properly to produce a good quality coating.

Initial attempts at electrocoating panels produced films that contained an excessive amount of film imperfections. When all the proper equipment was in place and operating we mixed two E'coat baths containing the standard BASF formulation and began processing panels. One bath was made from the pigment paste produced by BASF while the other bath was made from the pigment paste produced at NAWC. Several problems associated with the E'coat bath and the rinse stage caused the majority of the film defects.

Small defects which appear as bumps or intact bubbles cover the panels. Shortly before these panels were processed we received E'coated panels from Mac-Air. Their panels were much better

than the panels produced from either of the two baths here at NAWC. The Mac-Air panels may have one or two of the small defects on an entire 3 x 6 inch panel while our panels had several dozen per square inch.

Also, the stability of the two E'coat baths containing the standard BASF formulation did not meet manufactures requirements. After three weeks of continuous mixing during which time no panels were processed an excessive amount of particulate matter was recovered from the #325 mesh sieve. These problems need to be corrected before any formulation work can continue.

2.6.2 Incorporate Pigments into Electrocoat Materials. The primary task for our group is the formulation of corrosion inhibiting pigments into E'coat materials. Typically, E'coat baths are made from two separate feedstocks. Our formulation work will concentrate on introducing different pigment dispersions into the resin paste. The resin emulsion will be used as received from the supplier.

Producing this pigment dispersion requires the development of the correct grinding technique. This quarter we worked on the technique using the standard color pigments (i.e. TiO_2) used by BASF. After this technique is developed, the formulation work may advance to incorporating corrosion inhibitors. The equipment originally available at NAWC could not provide the required fineness of grind, which is between a 7 and a 7.5 on the Hegman gauge.

2.6.3 Obtain Access to Anodic Electrocoat Materials. All formulation work performed to date used a single cathodic E'coat material as the basis for the formulation work. The automotive industry prefers cathodic materials because they form a better barrier and so provide improved corrosion protection. However, the ZDOC program may benefit from the slightly reduced barrier properties provided by anodic E'coat materials. The reduced barrier properties may allow the corrosion inhibiting pigments to leach out into any defect areas and so provide protection. Cathodic materials may be such good barriers that the inhibitors are encapsulated in the coating so tightly that they are unable to leach out to provide protection.

A non-disclosure agreement is in place between NAWC and PPG. NAWC provided PPG with their proprietary, corrosion inhibiting, pigment formulations. PPG will determine which packages appear to offer the best chance of compatibility with their E'coat materials, primarily their anodic products. NAWC also requested that PPG provide samples of their E'coat for our in house process line. However, PPG appears unwilling to provide this level of support so, the NAWC E'coat process line may be limited to formulating with cathodic materials for the duration of the ZDOC program.

2.6.4 Qualify Pigment Dispersions. Using a microscope to size and count the particles is a popular method of characterizing pigment dispersions. NAWC has a video microscope/image processing system available that may be capable of performing this work. We feel it is worthwhile to commit some time to determine if this system is capable of correctly identifying the dispersed pigments in the E'coat materials.

3.0 GENERAL METHODOLOGY

3.1 Photocurable Coatings

3.1.1 Screening Testing on Photocurable Coatings. During this quarter, testing continued on the most promising materials evaluated to date. In addition a contract was issued to the Naval Surface Warfare Center (NSWC) to continue promising work being performed by

Barbara Howell on low toxicity, UV curable paints for use on submarines. The suppliers and the candidate materials on which testing is continuing are listed in Table II in Appendix A.

3.1.2 Incorporation of Non-toxic Corrosion Inhibiting Pigments. All ingredients for each of NAWC's corrosion inhibiting pigment formulations have been obtained from the manufacturers. The UV transmission of each of these NAWC pigments have been obtained when mixed in a glycerol base. Incorporation of the nonchromated corrosion inhibiting pigments was begun in this quarter. The milling process was also investigated during this quarter. During the screening phase, all candidate materials were applied to the Mil-C-5541 conversion coated 2024 T3 aluminum baseline substrate. Incorporation of these pigments will continue by HAC-TSD and selected paint suppliers. These materials will be tested for coating properties. Formulations will be optimized based on results obtained during this phase.

3.2 Inhibitor Modeling and Characterization

3.2.1 Modeling. A sample model was designed and a resin system selected to study the mechanism of corrosion inhibitors. The system selected was Epon 828, a epichlorohydrin bisphenol A resin and Epicure 3140, a polyamide curing agent, both manufactured by Shell. This formulation represents a 100% solids mixture. The model consists of a film formed by spin coating the activated resin mixture onto a chromium conversion coated 2024-T3 aluminum panel. By controlling the spin time we were able to obtain reproducible film thicknesses. A polycarbonate Isopore filter with a known pore size was compressed into the resin to form a laminate consisting of a resin layer sandwiched between the aluminum substrate and the filter. The purpose of the filter was to provide a uniform and controlled method for exposing the resin to the electrolyte. The laminate, consisting of the filter, resin, and substrate was allowed to cure for seven days and impedance measurements were made by placing an o-ring cell over the filter and using a 0.1 M K_2SO_4 electrolyte solution.

3.2.2 Chromate Conversion Coating Evaluation. Three meetings were held at Warminster to coordinate this work on conversion coatings with other members of the team and several interesting approaches to evaluate the coatings were tried. As a first step several candidate testing procedures were selected by searching the literature and on the advise of in house NAWC workers. Each method selected was evaluated with respect to its ability to distinguish between conversion coated aluminum samples of low (below mil spec.), middle (within mil spec.) and high (above mil spec.) coating weights. Those methods surviving the first round of the study are further investigated. The samples for this study are produced at NAWC specifically for each round of the investigation.

3.2.3 Electrochemical Impedance Spectroscopy. Commercially available E'coat and powder coat materials are investigated and characterized to provide background information. The work is extended to developmental coatings and/or model systems where appropriate. The characterization of a coating is approached by first mathematically modeling the impedance spectra using equivalent circuits. Then, plausible physical models are tested by measuring the effect on the impedance spectra of varying testing parameters.

3.3 Powder Coating Non-conductive Substrates

Appendix B contains the technical paper prepared for the TMS annual meeting. This paper summarizes much of the work performed to date and discusses the methodology used for evaluating the coatings applied to non-conductive substrates. Specifically, the work performed through October 1994 through December 1994 to characterize the voids forming in the epoxy coatings is discussed in detail.

3.4 IR Curing of Powder Coatings

The IR oven was profiled to determine the required settings to obtain the substrate surface temperatures needed to obtain a full coating cure. Steel panels were instrumented with thermal couples and processed through the IR oven to obtain thermal profiles of the substrate surface. The instrumented panels were then powder coated and processed through the oven since the emissivity of the coated panels would be slightly different than the bare steel panels. The profile was then complete and the required IR oven settings determined. An MEK wipe was used to determine the extent of cure on the coated substrates to insure a full cure was obtained.

3.5 Powder Coating Development

The test plan for development of inhibited powder coatings development has been documented and reported in earlier reports. This test plan was used by both NAWC and HMSC to test the powder coatings formulations under evaluation. The first iteration of powder coatings testing has been completed. The test results have been compared and documented. NAWC has utilized a total performance evaluation method to evaluate the performance of inhibited coatings versus non-inhibited coatings. This methodology is based on weighting factors where the most important properties of the coating are weighted more than the less important properties. This weighting is determined by "experts" in the field of protective coatings.

3.6 Electrocoat development

Before any formulation work can begin we must develop the techniques and the industrial art for operating an E'coat process line. An in house effort formulating electrocoat materials containing non-toxic, corrosion inhibiting pigments is a multistep process.

First, each stage of the process line must operate properly to produce a good quality coating. Once the process line is operating properly with commercially available materials we may then begin to produce our own feed materials. Our formulation work will concentrate on introducing different pigment dispersions into the resin paste.

A typical E'coat bath is made from two separate feedstocks. The bulk of the resin is supplied to the bath as an emulsion that does not contain any pigments. The pigments, whether for color or corrosion protection, are introduced to the bath as a separate feed stream. This stream consists of the pigments and other powder additives dispersed throughout additional resin.

Producing this pigment dispersion requires the development of the correct grinding technique. This technique consists of more than assembling the correct equipment and turning it on to mix. These dispersions require the correct viscosity and flow pattern during the dispersion process. Additions of the pigment and later of water or other solvent to aid the process are best determined by previous experience. Once the techniques for producing the standard pigments paste are developed other corrosion inhibiting pigments may be attempted.

4.0 TECHNICAL RESULTS

4.1 Photocurable Coatings

4.1.1 Supplier Summary. Table II, shown in Appendix A, shows the candidates still in consideration. Table IV, shown in Appendix A, shows the latest screening test results of the candidates materials submitted for consideration.

4.1.1.1 Sokol Enterprises Photocurable Coating. Sokol Enterprises has been developing a line of coatings which are 100% solids and are being targeted for the automotive industry (see Ref. 1). The very low (sprayable) viscosity of this material makes them particularly unique among candidates evaluated to date. Of the nine different formulations submitted by Sokol Enterprises, the best candidate, Sokol 1516, was pigmented with pigment formulation Z14L. The adhesion of the pigmented formulation was much worse than the excellent adhesion exhibited as a clearcoat. FTIR analysis of the film showed a full cure which means the probable UV opacity of the pigment formulation may or may not be the cause. Further investigation is underway of this failure. Unlike the other suppliers, Sokol has very little experience formulating pigmented, military specification paints. Therefore, Hughes needs to give formulation guidance to Sokol to assist in improving the performance properties of the 1516 product.

4.1.1.2 3M Dual Cure Coating. The 3M Corporate Research Lab has been working on a dual cure, photocurable, coating for several years under a DOE project (Contract No. AC04-88ID12692). The goals of this program were similar in many ways to the ZDOC program with several exceptions. 3M was evaluating a primer/topcoat system and was not evaluating a nonchromated corrosion inhibiting primer. The 3M submittal is a urethane/acrylate formulation with titanium dioxide pigment (designated "3M Dual Cure Polyurethane Coating" in Table 2) and contains 340 g/l VOC. A clearcoat was also submitted to enable incorporate of the pigments used in this program. One of the ingredients of the formulation is sensitive to shear stresses and was not able to survive ball milling. Therefore, 3M submitted a three part kit to avoid this problem. Ball milling was unsuccessful due to the high viscosity of the grind resin. This problem is normally avoided by adjusting the viscosity of the grind resin with solvent. In this case the problem could not be solved in this manner as both components suitable as a grind base were too high in viscosity. Unfortunately, the viscosity of the grind is too low for the laboratory 3 roll mill. Further investigation of this milling problem is in progress.

3M representatives had previously agreed to continue work on their formulation to further reduce the VOC content. The formulation includes VOC's in a letdown solvent (which was not included in the unpigmented formulation submitted) and also in a resin component. Since the DOE contract was completed, 3M has decided not to continue the search for a solvent-free resin. 3M also has elected not to release the formulation preventing Hughes from continuing the effort. The VOC of the existing formulation is slightly over 120 g/l which is a significant improvement over the current 340 and 420 g/l paints in industry. Work will continue to successfully find a means to grind the corrosion inhibiting pigments into the formulation.

4.1.1.3 Miles Laboratories. In the literature it was established that Miles Laboratories was very active in producing paints with a lower environmental impact. The Miles Defense Sector has a significant formulation capability and has worked extensively on ultra low VOC military topcoats for ZDOC team member NAWC. In the literature and at the Radtech UV convention it was establish Miles' Wood Products Sector has been making very significant progress on zero VOC, waterbased, UV curable coatings for wood products. For these reasons it appeared Miles Laboratories would be a valuable contributor of products for testing on this program. Late in the 4th quarter of this program, Miles submitted a waterbased, conventionally cured, polyester/acrylate coating for evaluation. This submittal did not wet the conversion coating aluminum sufficiently and had poor impact resistance. At this point Miles decided not to continue participation in this program because an analysis indicated the market for this product was insufficient to justify the significant effort deemed necessary to combine the technologies of the Defense and Wood Products Sectors to produce a paint suitable for testing. The Defense Sector was working on conventionally cured, low VOC coatings and the Wood Products Sector was working on waterbased, UV curable wood coatings. The idea of considering non-UV cured, ultra low VOC coatings in this program was determined inappropriate.

4.1.1.4 Dymax Corporation. The Dymax formulation with the most promising properties, X256-16-1, is based on UV curable conformal coating technology for electronic circuit boards. This urethane/acrylic copolymer cures in the UV light and in shadows with a secondary cure mechanism using atmospheric moisture. Pigmenting this formulation will occur in the next reporting period after questions regarding the opacity of the pigments has been resolved.

4.1.1.5 Herberts. Herberts, Inc. is a producer of powder coatings and is working with HAC-MSG in the powder phase of this program. Herberts also has produced a unique formulation that fuses at an ultra low 160 °F and is UV curable. This combination of properties could be extremely useful for temperature sensitive substrates that cannot withstand the 250 to 350 °F fusion temperatures of most commonly seen low temperature powders. Initial submittals did not meet impact flexibility requirements. In this past quarter several other submittals again were deficient in flexibility. Kevin Biller of Herberts had been attempting to improve flexibility by adding plasticizers and flexibilizers to the Ciba-Geigy resin system he was using. This month he decided to depart from this strategy and use a different base resin system. He will evaluate new resin systems submitted by Herbert's Switzerland headquarters. His schedule calls for receiving these new resins by 2/1/95. New formulations should be available for testing in February.

4.1.2 Screening Test Results. The screening tests selected and test results are included in Table IV in Appendix A. These tests were performed in-house on specimens coated 2-2.5 mils thick. Table III, included in Appendix A, shows a comparison of screening test results for Sokol 1516 with pigment and without pigment. Conversion coating 2024 T3 aluminum was used as the substrate for all specimens. Primer was not used on any of the panels.

4.2 *Inhibitor Modeling and Characterization*

4.2.1 Modeling. Initial results have confirmed the viability of the experimental design described in Section 3.2.1 and work is underway in evaluating selected inhibitors. Efforts will concentrate on readily available commercial inhibitors.

4.2.2 Chromate Conversion Coating Evaluation. This quarter we completed the first round of the project investigating alternate methods of analyzing the quality of chromate conversion coating pretreatments on aluminum. This round was designed to eliminate those tests incapable of distinguishing between different weight coatings. Unfortunately, a bath in the coating line was contaminated so every weight severely failed the one week salt fog test. The pendulum hardness test was found incapable of any differentiation between coating weights and was dropped from further study. All of the other tests will be reevaluated to some degree for the second phase of this project due to concerns over the effect the bath contamination may have had on the results. One method for determining the quality of conversion coatings involves a simple liquid drop test and a modification of the Snodgrass procedure to provide a rapid method of determining the uniformity and weight of a conversion coated 2024-T3 aluminum panel.

4.2.3 Electrochemical Impedance Spectroscopy Testing.

4.2.3.1 Activation. The impedance spectrum of an electrode removed from SO₂ salt fog can be changed from capacitive to multiple time constant behavior by activation. Previously it had been found that measured impedance spectra of E'coated chromated aluminum depends on the "activation" procedure used prior to the impedance measurement. In general, activation involves subjecting the painted electrode to the same stimulus used to measure impedance, except that a certain DC bias potential is used. An effective bias potential is determined experimentally.

Additional study of activation this quarter has lead to several conclusions.

- Activation does not change the impedance spectrum of a true capacitor (e.g. a freshly prepared electrode).
- The impedance spectrum of an electrode removed from SO₂ salt fog can be changed from capacitive to multiple time constant behavior by activation.
- The electrolyte plays a role in determining the effective bias potential to use. Capacitive electrodes in 3.5 % NaCl could be activated with relatively positive or negative potentials. A boric acid/borate electrolyte required relatively negative potentials while no effective potential could be found with distilled deionized water as the electrolyte.

4.2.3.2 Electrode Potential. Studying the effect of electrode potential on the impedance spectra should distinguish interfacial time constants from coating time constants. Electrode potential was found to have an effect on the impedance spectra. The effect can be as great as to convert a three time constant response to an apparent one time constant response.

4.2.3.3 Electrolyte. Preliminary work with boric acid/borate buffer indicates two time constant behavior in contrast to the three time constants observed in 3.5% NaCl. Further work on this point will help to complete the characterization of E'coats degraded in SO₂ salt fog.

4.3 Powder Coating Non-conductive Substrates

The results of the characterization of the voids formed in the coatings when using antistats on non-conductive substrates are contained in Appendix B. In addition, the technical paper summarizes the work to date performed on characterizing antistats for use in enhancing the surface conductivity of non-conductive substrates.

4.4 IR Curing of Powder Coatings

Appendix C contains the results of paint cure versus IR oven settings obtained during profiling of the IR oven. In addition, the oven profile curve is included. From these results, the desired surface temperature can be achieved to insure a full cure of the powder coating. These results will be used to process substrates to test the coating properties when cured with IR.

4.5 Powder Coating Development

Appendix D contains the test data for the first iteration of powder coatings tested by both NAWC and HMSC. Also included is a comparison table illustrating the differences in test results. Table I provides the description of the various coating systems and Tables II and III show the test data from NAWC and HMSC respectively. Table IV in Appendix D compares the test results from both NAWC and HMSC.

Corrosion inhibited and non-corrosion inhibited formulations, based on epoxy and acrylic powder coatings from Herberts Powder Coatings, Inc. and epoxy, epoxy-phenolic, acrylic, and low temperature epoxy powder coating from Morton International, have generally displayed good adhesion, chemical resistance, and humidity resistance on both aluminum and steel substrates. Flexibility has been generally low or deficient. The Morton epoxy-phenolic series has been an exception to this generalized flexibility trend with flexibility values that are characteristic of military aerospace primers and topcoats. Long term corrosion resistance testing is in progress.

Table V in Appendix D shows the weight factors applied to the test results reported by NAWC. This Total Performance Evaluation (TPE) method was used to evaluate and compare the performance characteristics with a resulting numerical value. The results of the evaluation are

shown in Table VI in Appendix D. The TPE results show that the inhibited powder coatings performed better than the non-inhibited coatings as determined by the final numerical value received. Based on the results shown in Appendix D, a second iteration of powder coatings is under development. This second iteration will attempt to increase the performance of the various inhibited coatings based on the results obtained from the first iteration.

4.6 Electrocoat development

4.6.1 Electrocoat Process Line. Initial attempts at controlling bath temperature using a hot plate proved inadequate. A dedicated temperature control system provides a quick and simple way to bring the E'coat bath to the proper operating temperature and maintain it during processing. The system selected for our use consists of a 22 liter water tank which securely fits over a 12 x 12 inch magnetic stirrer and a digital immersion circulator. The circulator provides both the actual heating and the water bath circulation in a single unit clamped to the side of the water tank.

Next, a problem developed with the Nalgene tanks used for the E'coat baths. The tanks were rapidly wearing and contaminating the bath under the constant agitation from a magnetic stirrer. After stirring for 7 to 10 days we noticed a chalky substance floating on top of the bath. Upon examining the tanks we discovered that the Teflon stir bar appeared to be wearing the tank bottom and depositing material into the bath. After several consultations with the tank supplier it was determined that the material of construction was inadequate for this process. Therefore, the polypropylene tanks were replaced with high density polyethylene tanks.

Initial attempts at electrocoating panels produced films that contained an excessive amount of film imperfections. Several problems located in the E'coat bath and the rinse stage caused the majority of the film defects.

A better filtration scheme prior to each panel processing session vastly improved the coating quality almost to the level of the Mac-Air panels. Some slight difference between our coatings and theirs is expected since they use continuous filtration for their 100 gallon tank. Previously our bath was filtered through a # 200 mesh sieve. Now the bath is first passed through a # 325 mesh sieve and then through a bag filter of the same type used by Mac-Air.

During the investigation into the cause of the small defects present on our panels several other process improvements became evident. These improvements involve the handling of the panels between the actual coating and the oven curing. A freshly coated panel is first immersed in a container of distilled, deionized water and soaked for approximately one minute. Then the panel is removed and rinsed under the deionized water faucet and hung to drain. When most of the water has drained (about 5 minutes) any remainder is blown off using compressed, oil-free nitrogen and then the panel is ready for curing.

The long term stability problem may be caused by an insufficient amount of acid available for the E'coat resin. The amount of available acid controls the degree of resin solubilization, called total neutralization (TN%) by the E'coat industry. This factor must be determined for individual baths. Measuring the pH does not provide an accurate representation of the TN% character of the bath material. To properly determine the TN% requires a potentiometric titration for both the acidic and basic milliequivalents, MEQa and MEQb respectively. We have established the procedures necessary to perform the non-aqueous, potentiometric titrations to determine the total neutralization of the resin in E'coat materials.

4.6.2 Electrocoat Pigment Dispersions. Additional accessories are available for the Dispermat high speed dissolver that allows us to grind the pigment paste in the same manner as BASF. After several attempts at processing a batch of paste, these accessories worked very well at reproducing the standard BASF pigment paste formulation. The final fineness of grind of greater than 7.5 on the Hegman gauge was reached in approximately one and a half hours. Typically, we process a 400 gram batch of pigment paste in a water jacketed, 500 ml vessel using

120 ml of ZrO beads and a dual-disk impeller. The only problem is the excessive loss of material, approximately 125 grams, due to sample testing and separating the beads.

5.0 IMPORTANT FINDINGS AND CONCLUSIONS

5.1 Photocurable Coatings

5.1.1. A contract has been granted to Barbara Howell of NSWC to continue her work on UV curable paints. Her previous work had resulted in a Navy gray, epoxy based paint cured with a xenon lamp for touchup painting on a submarine. This contract will add an in-house formulation capability to the effort to develop a zero VOC, UV curable paint for aluminum. Barbara's formulation strategy will be to switch from epoxy to polyurethane chemistry for this contract due to the increased flexibility requirements. Initial test submittals indicate improved flexibility is needed.

5.1.2. Miles and 3M have elected not to submit new candidates for testing on this program. Miles decided the potential market was insufficient to justify the needed research. 3M's DOE contract was completed and decided not to commit company funds on this research due to the limited market potential.

5.1.3. Herberts is continuing to submit UV cured powder paints for testing. A new resin system will be used to improve impact resistance.

5.1.4. Pigmenting the clearcoats has been problematic. The option of using solvent to adjust grind viscosity is not appropriate for a ZDOC type of paint. Adhesion of the pigmented Sokol 1516 to the conversion coated aluminum substrate was much worse than for the clearcoat despite a high degree of UV cure.

5.1.5. The UV transmission of the nonchromated corrosion inhibiting pigments is poor when the pigments are mixed into a glycerol vehicle. Tests will be repeated for pigments milled to a suitable grind before transmittance testing.

5.1.6. Sprayable coating with no VOC will be a challenge.

5.2 Inhibitor Modeling and Characterization

5.2.1. Positron studies on the resin system being used have provided a profile of the free volume of the cured resin in relation to the film thickness. It has been observed that the free volume is effected when the resin system is compressed during cure.

5.2.2. An E-coating formulation has been identified that can be synthesized at room temperature and in which inhibitor formulations can be incorporated for evaluation. This system will provide the ability to formulate resins with known compositions.

5.2.3 Activation of electrocoated aluminum electrodes is often needed in order to obtain useful impedance spectra.

5.2.4 The stationarity requirement for the interpretation of impedance spectra is satisfied for some of the degraded E'coated specimens studied.

5.2.5 Variation of EIS parameters such as electrolyte and electrode potential shows promise for determining physical models.

5.2.6 NAWC and Lehigh University completed the first phase of an effort to develop a method to analyze the quality of chromate conversion coating pretreatments on aluminum. Problems with a contaminated bath may have interfered with the results.

5.3 Powder Coating Non-conductive Substrates

5.3.1 Voids are forming in the coatings applied to non-conductive substrates treated with antistats to enhance the surface conductivity. The voids are formed primarily from the polymeric substrate but the antistat does contribute to some void formation. The voids do not effect the physical performance of the coating.

5.4 IR Curing of Powder Coatings

5.4.1 Powder coatings can be cured using IR energy. Required cure time and temperature is approximately 410°F for 90 seconds. The coating physical properties must still be tested.

5.5 Powder Coating Development

5.5.1 The inhibited powder coatings performed better than the non-inhibited coatings as determined by a Total Performance Evaluation method. A second iteration of inhibited coatings is under development.

5.5.2 Corrosion inhibited powder coats display good adhesion, chemical resistance, and humidity resistance on both steel and aluminum. Flexibility has been low or deficient. Long term corrosion resistance testing is in progress.

5.6 Electrocoat Development

5.6.1 Work is continuing on the establishment of an in house E'coat process line. This quarter we finished assembling the equipment and established the proper operating procedures. The E'coats produced in this line are nearly as free of imperfections as those produced by Mac-Air in their 100 gallon tank.

5.6.2 Finished developing the technique of grinding a pigment paste that reproduces the standard BASF formulation. This required obtaining additional equipment and experience before producing properly dispersed pigment pastes.

5.6.3 Established a non-disclosure agreement between NAWC and PPG. NAWC sent PPG with their non-toxic, corrosion inhibiting, pigment packages for incorporation into their E'coat materials. PPG is evaluating the compatibility of the pigment packages with their E'coat materials, primarily their anodic products.

6.0 SIGNIFICANT HARDWARE DEVELOPMENTS

N/A

7.0 SPECIAL COMMENTS

N/A

8.0 IMPLICATIONS FOR FURTHER RESEARCH

N/A

9.0 REFERENCES

N/A

ZERO DISCHARGE ORGANIC COATINGS

Powder Paint - UV Curable Paint - E-Coat

Appendixes

Appendix A	UV Curing of Powders -Test Results
Appendix B	Powder Coating of Non-conductive Substrates
Appendix C	IR Cure Profile Results
Appendix D	Powder Coating Development Test Results

APPENDIX A

UV Curing of Powders

Test Results

	iMolywhite	iSicorin	iPhosplus	iItohou	Halox	ZWP	iSicorin	Halox	Mix (3)	iSicorin	Itohou
Concentration	0.14	0.1	0.1	0.13	0.11	0.1	0.2	0.31	0.3	2	2
Wavelengths											
450	60.3	57.5	100.0	64.6	57.5	66.1	38.0	23.4	33.9	0.35	0.36
440	60.3	55.0	100.0	63.1	56.2	66.1	36.3	22.9	33.1	0.34	0.35
430	61.7	53.7	100.0	63.1	56.2	66.1	34.7	22.4	32.4	0.32	0.34
420	61.7	52.5	100.0	63.1	55.0	64.6	32.4	21.9	31.6	0.30	0.32
410	63.1	50.1	100.0	63.1	55.0	64.6	30.9	21.4	30.9	0.29	0.31
400	63.1	49.0	100.0	63.1	53.7	64.6	28.8	20.9	29.5	0.26	0.29
390	63.1	46.8	100.0	63.1	53.7	63.1	26.9	20.4	28.8	0.21	0.26
380	63.1	44.7	100.0	64.6	53.7	63.1	24.5	20.0	27.5	0.14	0.07
370	64.6	41.7	100.0	66.1	55.0	64.6	21.9	21.4	26.3	0.07	0.06
360	64.6	38.9	100.0	67.6	55.0	64.6	19.5	21.4	24.5	0.03	0.07
350	64.6	36.3	100.0	67.6	55.0	64.6	17.0	20.9	22.9	0.00	0.08
340	66.1	33.1	100.0	69.2	55.0	64.6	14.1	20.9	20.9	0.00	0.09
330	66.1	28.8	100.0	69.2	55.0	64.6	11.5	20.4	19.1	0.00	0.09
320	66.1	25.1	100.0	69.2	55.0	63.1	9.1	20.0	17.0	0.00	0.10
310	67.6	24.0	100.0	69.2	53.7	63.1	7.9	19.5	16.2	0.00	0.10
300	67.6	24.0	100.0	69.2	53.7	63.1	7.8	19.1	15.8	0.00	0.10
290	69.2	24.5	100.0	70.8	52.5	63.1	8.1	18.6	16.6	0.00	0.10
280	69.2	25.7	100.0	70.8	52.5	63.1	8.7	18.2	17.0	0.00	0.10
270	69.2	25.7	100.0	70.8	51.3	61.7	9.1	17.8	17.0	0.00	0.09
260	69.2	24.5	100.0	70.8	50.1	60.3	8.5	17.0	16.6	0.00	0.09
250	70.8	22.4	100.0	70.8	50.1	60.3	7.2	16.2	15.1	0.00	0.09

Table I. Percent Transmittance of UV Energy. A sample of pigment(s) of the indicated concentration was mixed into a UV transparent carrier (glycerol). The pigment dispersions were placed in a quartz cell with a 0.1 cm path length and tested in a Varian Cary Model 2300 UV-VIS-NIR spectrophotometer. Low transmittance values were observed throughout the frequency range tested. Photoinitiators for curing the coatings are typically in the 350 to 400 wavelength range. Pigments tested are ingredients of NAWC's Nonchromated Corrosion Inhibiting formulations to be used on this program. "Mix" is formulation Z-14L.

**UV CURABLE COATING CANDIDATES
EXPOSED TO SCREENING TESTS
(ZDOC PROGRAM)**

Material & manufacturer	Material Type	Appx. viscosity (cps)	Specific gravity	VOC content (g/l)	Pigmented?	Comments
Caschem	urethane/acrylate	150	N/A	0	no	modified conformal coating
Sokol 1189	urethane/acrylate	225	TBD	0	no	specialty formulation
Sokol 908-15	urethane/acrylate	300	TBD	0	no	specialty formulation
Sokol 15XX series	urethane/acrylate	300	TBD	0	no	specialty formulations. 1516 is leading Sokol candidate. Properties were reduced when pigmented with formulation Z-14L.
3M gloss white	urethane and acrylic	TBD	TBD	388	white	From DOE contract
3M 631 clear	urethane and acrylic	1000	1.2	120	no	Three component. Viscosity is too high to properly ball mill.
NSWC epoxy	epoxy	TBD	TBD	0	gray	
NSWC polyurethane	polyurethane	TBD	TBD	0	gray	New formulation being submitted with improved adhesion to aluminum. Some compatibility problems are being experienced as evidenced by uneven coating appearance.
Millies 3919	polyester/acrylate	140	TBD	18	no	Contains water
Dymax 986	urethane/acrylate	100	1.07	0	no	modified conformal coating
Dymax 984 TC	urethane/acrylate	150	1.05	0	no	modified conformal coating
Dymax X256-16-1	urethane/acrylate	160	1.05	0	no	specialty formulation
Herberts UV powder	080-25-1	N/A	1.96	0	white	Unique UV curable, powder coating with a very low, 160 °F fusion temperature. A new formulation based on more flexible resin chemistry is being developed.
Hardman	epoxy/acrylate	TBD	TBD	0	no	off the shelf product
PD George RO-661	acrylic	TBD	1.17	0	no	off the shelf product
Micro-Lite 3010M	urethane/acrylic	50	0.98	0	no	Modified conformal coating

Table II. Materials and suppliers submitting samples for evaluation. Leading candidates evaluated to date in **bold**. See comments column for latest status.

SCREENING TESTS FOR PHOTOCURABLE COATINGS

Coating Designation: Sokol 1516 with and without Z-14L pigment

Manufacturer: Sokol, pigment milled at TSD

Color: White, translucent

Cure Schedule: UV, 5 FPM, 3 passes

Measured Coating Thickness: 1.9 to 2.3 mils

Comments: Z-14L pigment formulation at a PVC of 27.6

Test	Description	Requirement	Result Unpigmented	Result Pigment
Dry Tape Adhesion	3M 250 tape	No delamination	Pass	Failed
Wet Tape adhesion	24 hour immersion	No delamination	Pass	Failed
Impact Flexibility			forward: 26 in-lb. reverse: 4 in-lb.	forward: 2 in-lb. reverse: 2 in-lb.
MEK Resistance	50 wipes	No removal of coating	Pass	pass
Pencil hardness			4H	SH
Skydrol 500 Resistance	7 day immersion	<2 pencil hardness change	4H	Fail. Coating delaminated in soln.
Lube Oil resistance (Mil-L-23699)	24 hour, 250 °F	pencil hardness, appearance	NT	Fail. Coating delaminated in soln.
Hydraulic fluid resistance (Mil-H-83282)	25 hour, 150 °F	pencil hardness, appearance	NT	Fail. Coating delaminated in soln.
JP-5 Jet fuel	7 day, RT	pencil hardness, appearance	NT	NT
Salt fog (5%)	1000 hours	no corrosion	NT	NT
Flexibility (conical mandrel)		No cracking at 1/4"	Pass	Fail
Gloss (60°)			108.6	34.2
Heat resistance	4 hours at 300°F	meet gloss and impact requirements	111.4 Forward: 50 in/lb. Reverse: 44 in-lb.	16.3 Forward: 2 in-lb. Reverse: 2 in-lb.

Table III. Effect of Nonchromated Corrosion Inhibiting Pigment. Sokol Industries' Sokol 1516 was subjected to screening tests before and after addition of 27.6 PVC of Z-14L pigment. Pigment was ball milled into 1516 to a Hegman grind of 6. Pigmented coating properties are significantly reduced by the pigmentation.

ZDOC SCREENING TEST RESULTS UV CURABLE COATINGS

Test	Test Description	Requirement	Microlite 3010	Caschem	3M Dual Cure Polyurethane Coating	NSWC epoxy	NSWC polyurethane
Thickness (mils)			1.5	3.0	2.5	1.2-3.4 mils	1.2-3 mils
Color	Visual	N/A	Clear	Clear	White	Gray	Gray
1. Dry Tape Adhesion	1. 3M 250 tape	No delamination	FAIL	FAIL	FAIL	FAIL	FAIL
2. Wet Tape adhesion	2. 24 hour immersion	No delamination	FAIL	FAIL	FAIL	FAIL	FAIL
Impact (fwd) in-lb.	ASTM D2794	40% elongation	12 in-lb. (fwd)	4 in-lb (fwd)	80 in-lb. (fwd)	<10 in-lb (fwd)	<10 in-lb (fwd)
Impact (reverse) in-lb.			8 in-lb. (rev)	2 in-lb (rev)	>100 in-lb. (rev)	<10 in-lb (rev)	<10 in-lb (rev)
MEK Resistance	50 wipes	No removal of coating	PASS	PASS	PASS	PASS	PASS
Pencil hardness	ASTM D3363	none	7H	5H	4H	7H	6H
Skydrol 500 resistance	7 day immersion	<2 pencil hardness change	4H (PASS)	3H (PASS)	3H (PASS)	PASS	PASS
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	pencil hardness, appearance	appearance-good	appearance-good	appearance-good	not tested	not tested
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	pencil hardness, appearance	PASS	not tested	not tested	not tested	not tested
Salt fog (5%)	500 hours	no corrosion	Extensive corrosion	Extensive corrosion	Corrosion in scribe line only	Extensive corrosion	Extensive corrosion
Flexibility	Conical Mandrel	No cracking	FAIL	FAIL	PASS	FAIL	FAIL
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	115	PASS	91	86	85
Heat resistance	4 hours at 300°F	meet gloss and impact requirements	Gloss=100 16 in-lb (fwd) 4 in-lb (rev)	Gloss=95 4 in-lb (fwd) <2 in-lb (rev)	Gloss=90 >100 in-lb (fwd) 80 in-lb (rev)	Gloss=88 <10 in-lb (fwd) <10 in-lb (rev)	Gloss=77 <10 in-lb (fwd) <10 in-lb (rev)

Table IV. ZDOC UV Curable Coating Screening Results

Updated: January 17, 1995

Approved for public release; distribution is unlimited.

ZDOC SCREENING TEST RESULTS
UV CURABLE COATINGS
(cont'd)

Test	Test Description	Requirement	Miles 3919	3M 631	Dymax 986 Darc Cure	Dymax 984 TC	Dymax X256-16-1
Thickness (mils)			1.3	1.6	0.5	1.0	0.5
Color	Visual	N/A	clear	clear	clear	clear	clear
1. Dry Tape Adhesion	1. 3M 250 tape	No delamination	FAIL	PASS	FAIL	PASS	PASS
2. Wet Tape adhesion	2. 24 hour immersion	No delamination	FAIL	PASS	FAIL	PASS	PASS
Impact Flexibility	ASTM D2794	40% elongation	40 in-lb (fwd) 26 in-lb (rev)	80+ in-lb (fwd) 80+ in-lb (rev)	40 in-lb (fwd) 40 in-lb (rev)	20 in-lb (fwd) 20 in-lb (rev)	50 in-lb (fwd) 60 in-lb (rev)
MEK Resistance	50 wipes	No removal of coating	PASS	PASS	FAIL	FAIL	PASS
Pencil hardness	ASTM D3363	none	5H	3H	5H	9H	4H
Skydrol 500 resistance	7 day immersion	<2 pencil hardness change	4H (PASS)	3H (PASS)	PASS (3H)	PASS (7H)	PASS (4H)
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	pencil hardness, appearance	PASS (5H) appearance-good	PASS (3H) appearance-good	not tested	not tested	not tested
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	pencil hardness, appearance	PASS (5H)	PASS (3H)	not tested	not tested	not tested
Salt fog (5%)	500 hours	no corrosion	Extensive corrosion	Corrosion in scribe lines only	Extensive corrosion	Extensive corrosion	Extensive corrosion
Flexibility	Conical Mandrel	No cracking	PASS	PASS	PASS	FAIL	PASS
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	97	100	86	100	100
Heat resistance	4 hours at 300°F	meet gloss and impact requirements	Gloss=96 32 in-lb (fwd) 32 in-lb (rev)	Gloss=100 80+ in-lb (fwd) 80+ in-lb (rev)	Gloss=88 40 in-lb (fwd) 35 in-lb (rev)	Gloss=100 14 in-lb (fwd) 10 in-lb (rev)	Gloss=100 50 in-lb (fwd) 50 in-lb (rev)

Table IV. ZDOC UV Curable Coating Screening Results

Updated: January 17, 1995

Approved for public release; distribution is unlimited.

**ZDOC SCREENING TEST RESULTS
UV CURABLE COATINGS
(cont'd)**

Test	Test Description	Requirement	Sokol 1189 Coating	Sokol 908-15	Sokol 1510	Sokol 1511	Sokol 1512
Thickness (mils)				0.7	1.8	1.7	1.8
Color	Visual	N/A	clear	clear	clear	clear	clear
1. Dry Tape Adhesion 2. Wet Tape adhesion	1. 3M 250 tape 2. 24 hour immersion	No delamination	PASS	PASS	PASS	PASS	PASS
Impact Flexibility	ASTM D2794	No delamination 40% elongation	10 in-lb. (fwd) 4 in-lb. (rev)	<10 in-lb (fwd) <10 in-lb (rev)	10 in-lb (fwd) 2 in-lb (rev)	18 in-lb (fwd) 12 in-lb (rev)	16 in-lb (fwd) 2 in-lb (rev)
MEK Resistance	50 wipes	No removal of coating	PASS	PASS (slight removal)	PASS	PASS	PASS
Pencil hardness	ASTM D3363	none	5H	8H	4H	4H	4H
Skydrol 500 resistance	7 day immersion	<2 pencil hardness change	4H (PASS) appearance-good	7H	FAIL (flaked off panel)	FAIL (coating rmvd)	FAIL (flaked off panel)
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	pencil hardness, appearance	not tested	not tested	PASS	PASS	PASS
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	pencil hardness, appearance	not tested	not tested	PASS	PASS	PASS
Salt fog (5%)	500 hours	no corrosion	Extensive corrosion	Corrosion in scribe lines only	Corrosion in scribe lines only	Corrosion in scribe lines only	Corrosion in scribe lines only
Flexibility	Conical Mandrel	No cracking	PASS	PASS	PASS	FAIL	PASS
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	91	100	97	99	93
Heat resistance	4 hours at 300°F	meet gloss and impact requirements	Gloss=45 (FAIL) 6 in-lb (fwd) 4 in-lb (rev)	Gloss=100 <10 in-lb (fwd) <10 in-lb (rev)	Gloss =100 38 in-lb (fwd) 32 in-lb (rev)	Gloss =98 16 in-lb (fwd) 18 in-lb (rev)	Gloss =100 22 in-lb (fwd) 24 in-lb (rev)

Table IV. ZDOC UV Curable Coating Screening Results

Updated: January 17, 1995

Approved for public release; distribution is unlimited.

**ZDOC SCREENING TEST RESULTS
UV CURABLE COATINGS
(cont'd)**

Test	Test Description	Requirement	Sokol 1513	Sokol 1514	Sokol 1515	Sokol 1516	Sokol 1516 W/ Z-14L	Herberts UV Powder
Thickness (mils)			1.8	1.7	1.6	1.7	1.9	1.2-1.9
Color	Visual	N/A	clear	clear	clear	clear	white, translucent	white
1. Dry Tape Adhesion	1. 3M 250 tape	No delamination	PASS	PASS	PASS	PASS	FAILED	PASS
2. Wet Tape adhesion	2. 24 hour immersion	No delamination	PASS	PASS	PASS	PASS	FAILED	PASS
Impact Flexibility	ASTM D2794	40% elongation	24 in-lb (fwd) 22 in-lb (rev)	14 in-lb (fwd) 4 in-lb (rev)	30 in-lb (fwd) 24 in-lb (rev)	26 in-lb (fwd) 4 in-lb (rev)	2 in-lb (fwd) 2 in-lb (rev)	4 in-lb (fwd) 0 in-lb (rev)
MEK Resistance	50 wipes	No removal of coating	PASS	PASS	PASS	PASS	PASS	PASS
Pencil hardness	ASTM D3363	none	4H	4H	4H	4H	SH	4H
Skydrol 500 resistance	7 day immersion	<2 pencil hardness change	PASS	PASS	PASS	PASS	FAIL Delamination in solution.	FAIL
Lube oil resistance (MIL-L-23699)	24 hour, 250°F	pencil hardness, appearance	PASS	PASS	PASS	PASS	FAIL Delamination in solution.	PASS
Hydraulic fluid resistance (MIL-H-83282)	25 hour, 150°F	pencil hardness, appearance	PASS	PASS	PASS	PASS	FAIL Delamination in solution.	PASS
Salt fog (5%)	500 hours	no corrosion	FAIL	Corrosion in scribe lines only	Corrosion in scribe lines only	Corrosion in scribe lines only	NT	Corrosion in scribe lines and some other areas.
Flexibility	Conical Mandrel	No cracking	PASS	PASS	FAIL	PASS	FAIL	FAIL
Gloss (60°)	FED-STD-141, Method 6101.1	90 or greater	96	98	100	100	34.2	86
Heat resistance	4 hours at 300°F	meet gloss and impact requirements	Gloss = 100 38 in-lb (fwd) 44 in-lb (rev)	Gloss = 100 36 in-lb (fwd) 22 in-lb (rev)	Gloss = 100 42 in-lb (fwd) 34 in-lb (rev)	Gloss = 100 50 in-lb (fwd) 44 in-lb (rev)	Gloss = 16.3 2 in-lb (fwd) 2 in-lb (rev)	Gloss = 83 6 in-lb (fwd) 0 in-lb (rev)

Table IV. ZDOC UV Curable Coating Screening Results

Updated: January 17, 1995

Approved for public release; distribution is unlimited.

APPENDIX B

Powder Coating of Non-conductive Substrates

ELECTROSTATIC POWDER PAINTING OF NON-CONDUCTIVE SUBSTRATES

Arthur J. McGinnis¹, Srin Raghavan¹, Tiffany Lindstrom¹,
James Leal², and Don R. Martin²

¹The Department of Materials Science and Engineering
University of Arizona
Tucson, Arizona 85721

²Hughes Missile Systems Company
Tucson, Arizona

Abstract

A method to electrostatically powder coat non-conductive substrates has been developed. This method uses a thin coating of an aerosol antistat containing a fatty quaternary ammonium compound onto the substrate prior to powder painting. Microstructural analysis of the epoxy coatings has shown that gases are trapped within the coating causing voids. The formation of large voids with diameters as large as 50 μm appear to be due to water-vapor released from the non-conductive substrate during curing of the epoxy coating. Even with the voids within the epoxy layer, the coating on the antistat treated substrate passed military specifications for adhesion and solvent resistance.

Sponsored by
Advanced Research Projects Agency
Defense Sciences Office
Zero Discharge Organic Coatings
ARPA Order No. 9328/06
Issued by ARPA/CMO under Contract #MDA972-93-C-0020

Introduction

Regulations under the local, state, and federal government are restricting, if not eliminating, the use of solvent based paints in the aerospace industry. Volatile Organic Compound (VOC) emission and hazardous waste generation and disposal associated with solvent paints are beginning to seriously impact the painting of aerospace hardware. Aerospace companies began working with powder painting in the late eighties in order to reduce VOC emission.

In solvent based paints, the solvents are used to transport the pigments and resins over the surface to be painted. After the evaporation of the solvent, the resins and pigments are left and form the painted surface. Only a fraction of the applied material forms the dry paint film since the volatiles comprise a significant portion (30% to 80%) of the applied paint film (1).

In contrast, powder based paints are made of fine particles (25-50 μm) of blended resins and pigments which are used to coat the surface of the designed substrate. The powder is typically fluidized and applied to electrically grounded substrates by means of an electrostatic spray gun. In these guns, corona electrodes are set at high-voltage (60-100 kV) which ionize the air that charges the powders. The powder particles are attracted to and adhere to the grounded substrate until it can be transported to an oven. The part is then baked in an oven at temperatures ranging from 250 F to 400 F to cross-link the thermoset polymer paint particles. Powder paint has essentially no volatile components (less than 1%) (1).

Electrostatic powder painting is a self-limiting process. The grounded metal panel provides a zero potential surface with respect to the potential of the high voltage gun thus driving the positively charged paint particle toward the surface of the panel. As the paint layer thickens ($\sim 25 \mu\text{m}$ to $250 \mu\text{m}$) on the substrate, charges begin to build up on the surface of the paint layer and repels the oncoming charged paint particles. The potential of the charged surface of the paint layer increases and the potential difference between the corona gun and the surface of the paint layer decreases. Powder painting non-conductive substrates using traditional methods is not possible since the substrate cannot be grounded to prevent the initial buildup of charges on the substrate and cannot be maintained at a zero potential with respect to the powder gun (2).

Background

Various techniques could be used to powder paint a non-conductive substrate; these include placing a metal backing onto a non-conductive substrate, coating of the substrate with a conductive primer, and adding a conductive component into the resin from which the non-conductive substrate is made.

A non-conductive substrate can be powder painted if a metal panel is temporarily placed behind and in contact with the substrate providing a charge dissipation path. However, the mechanisms for charge dissipation does not work for complicated three dimensional objects with large surface areas, awkward angles and segments.

The use of conductive primers can provide a conductive layer. When the conductive layer is grounded, it facilitates charge dissipation and provides a zero potential surface relative to the gun. The use of conductive primers to enhance the surface conductivity of substrates is a popular method in industry. Conductive primers typically contain metal as well as carbon particles and may be organic or aqueous based. Conductive primers containing nickel have been widely used in the automobile industry. Applying water based conductive primers onto non-conductive substrates takes skill since metal particles in the

conductive primer are susceptible to settling and tend to slide down vertical surfaces (prior to drying) leaving areas with poor conductivity. Because of their high conductivity, conductive primers often result in the attenuation of RF signals and may not be acceptable in certain aerospace applications.

The practice of mixing conductive ingredients to the resin powder from which the substrate is cast has been discussed. A method for the electrostatic coating of a resin molding by mixing with the resin a complex of a specified polyether and an electrolyte salt (soluble in the polyether) has been patented (3). The complex could be made from adding 1 part lithium perchlorate and 4 parts methanol into 20 parts polyether with stirring to obtain a homogeneous solution and then removing methanol in vacuum. The drawback with this method is that the company doing the powder painting may not be in the business of making their own resins!

The use of antistatic materials to temporarily enhance surface conductivity has been widely discussed in many aspects of plastic processing. Typically antistats can be added to the resin to be casted. After casting, the antistats may migrate to the surface providing surface conductivity. Antistats can also be applied from a solvent using a brush-on or spray-on technique (4).

Since the use of non-conductive materials in many aerospace applications is increasing, techniques for electrostatic powder coating of non-conductive substrates are being actively investigated. The objective of this paper is to report the results of a surface conductivity enhancing method to enable powder coating of polymeric substrates.

Materials And Methods

A polyetherimide thermoplastic (Ultem1000[®]), a polyetheretherketone (VICTREX[™] PEEK) thermoplastic and glass were chosen as representative non-conductive substrates. The polymer samples were obtained from Polypenco Polymer Corporation. Ultem 1000 has a glass transition temperature of 217°C, while the PEEK substrate has a glass transition temperature of 248°C. The epoxy powder used for powder painting was obtained from Morton (Corvel[®] #10-7317). The recommended cure schedule for this epoxy powder is 171°C for 35 minutes.

To enhance the surface conductivity of the substrate, an aerosol of a fatty quaternary ammonium compound was used. A commercially available antistat spray containing dimethyl ditallow ammonium chloride was chosen for the investigations.

All powder painting experiments were carried out at the Hughes Missiles Systems site in Tucson, Arizona. The powder painting equipment, which included a spraybooth, gun, hopper and a powder pump, was made by Nordson. Since the experiments used flat panels, the charging voltage was set at 90 kV. In a typical experiment, a non-conductive panel was first treated with the antistat. The treated non-conductive panel was hung vertically in the spray booth using a metal clip that was attached to the grounded powder booth. It took roughly 2 to 3 seconds to powder paint a substrate. After painting, the painted panel was transferred to a rack until it was time to cure the epoxy coatings. The curing of the powder was done in a convection furnace at 171°C for 35 minutes.

There were concerns about volatiles within the non-conductive substrates and in the antistat. A Perkin-Elmer Thermogravimetric Analyzer (model TGA 7) was used to measure the weight loss of the substrates and the antistats during various heat treatments. A Hewlett Packard Gas Chromatograph/Mass Spectrometer (model HP 5995) was used to characterize the antistats and the out-gassing products from the non-conductive substrates during the curing process.

Whether an antistat treated substrate can be powder painted depends on the surface conductivity of the substrate. A Keithly Instruments resistivity adapter (model 6105) and Keithley Instruments electrometer/source (model 617) were used to measure surface resistivity of samples.

The morphology and the microstructure of the cross sections of the cured epoxy powder coating were characterized using a Hitachi Scanning Electron Microscope (model 2460N). The working distance was set at 25 mm and the samples were sputtered with Au-Pd.

The coatings were characterized for their adhesion and solvent resistance using standard military specification methods. For adhesion measurements, a modified ASTM adhesion tape test (ASTM D 3359, method A) was used. For the adhesion tests, the painted substrates were immersed in distilled water for 24 hours at 23°C. After immersion, two parallel scribes, 3/4 inch apart, were cut through the coating and into the substrate, and an "X" was subsequently scribed through the coating between the two initial scribes. A strip of 3M 250 masking tape was then applied firmly to the coating surface either perpendicular to or along the scribe lines and immediately removed with a quick motion. After peeling the tape, the adhesion was rated as shown in Table 1.

Table I ASTM D3359 Adhesion Ratings

<i>Rating</i>	<i>Description</i>
5A	No Peeling or removal
4A	Trace peeling or removal along incisions
3A	Jagged removal along incisions up to 1/16 in. (1.6 mm) on either side
2A	Jagged removal along most of incisions up to 1/8 in. (3.2 mm) on either side
1A	Removal from most of the area of the "X" under the tape
0A	Removal beyond the area of the "X"

The chemical (fluid) resistance test was intended to analyze the ability of the coating to resist common fluids used in aircraft. A coated non-conductive substrate would fail the fluid resistance test if panels displayed blistering or discoloration after being immersed in a specified solvent at a given time and temperature. Separate powder painted Ultem substrates were immersed in lubricating oil (MIL-L-23699) for 24 hours at 121°C, hydraulic fluid (MIL-H-83282) for 24 hours at 65°C and a hydrocarbon solvent (JP-4) for 168 hours at 25°C. Following immersion, the samples were taken out and optically inspected for blistering or discoloration.

Results and Discussion

Since the aerosol antistat is a commercial product, an attempt was made to identify the ingredients in the antistat. The analysis was carried out using GC/MS and the results are shown in Figure 1. The five peaks in Figure 1 may be identified as follows: peak #1 is ethanol (C_2H_5OH), peak #2 is isobutane (C_4H_{10}), peak #3 is tert-butyl alcohol ($C_4H_{10}O$), peak #4 is 4-Penten-2-ol ($C_5H_{10}O$) and peak #5 may be ascribed to 2-propanoic acid, 2-methyl-, and butyl ester. Ethanol is most likely the carrier solvent, and isobutane is most likely the propellant for the commercial aerosol antistat.

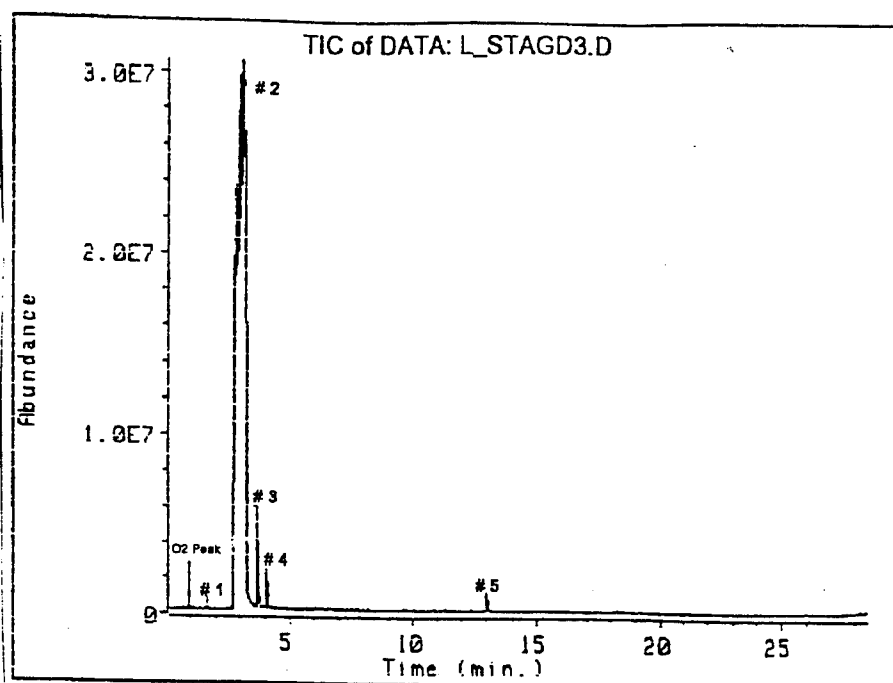


Figure 1 - GC/MS spectrum of aerosol antistat.

The next series of experiments were conducted to test the feasibility of powder painting glass slides (25x75x1 mm) using the aerosol antistat. In these tests, the glass slides were sprayed with the aerosol antistat and dried in an oven at a specified temperature for a predetermined time and then were powder coated. The antistat coating measured approximately 7.5 mg/cm² when freshly applied. After air drying for 30 minutes, the coating measured only 0.1 mg/cm² due to evaporation of propellant. The results of the powder coating were qualitatively evaluated after curing and ranked on a scale of 1 (bad) to 10 (good). A ranking of 10 indicates that coating was uniform and covered the glass slide entirely with no bare spots. A ranking of less than 10 indicates incomplete powder painting where the coating was non-uniform and had bare spots. The drying temperature was used as a variable to determine whether the antistat would cease to function as a conductivity enhancing agent above a certain temperature. The relative humidity in the laboratory during the experiment was low (roughly 30%).

The results of these tests displayed in Figure 2 show that at lower drying temperatures coating is possible even at long drying times. At higher temperatures, depending on the drying time, the coatings exhibited incomplete coverage. For example at 170°C, if the drying was done for longer than 20 minutes, the ranking of the coating was 4 or less. These preliminary tests indicated that it is possible to powder coat non-conductive substrates (glass) using the antistat and also that drying conditions may be critical for uniform coating.

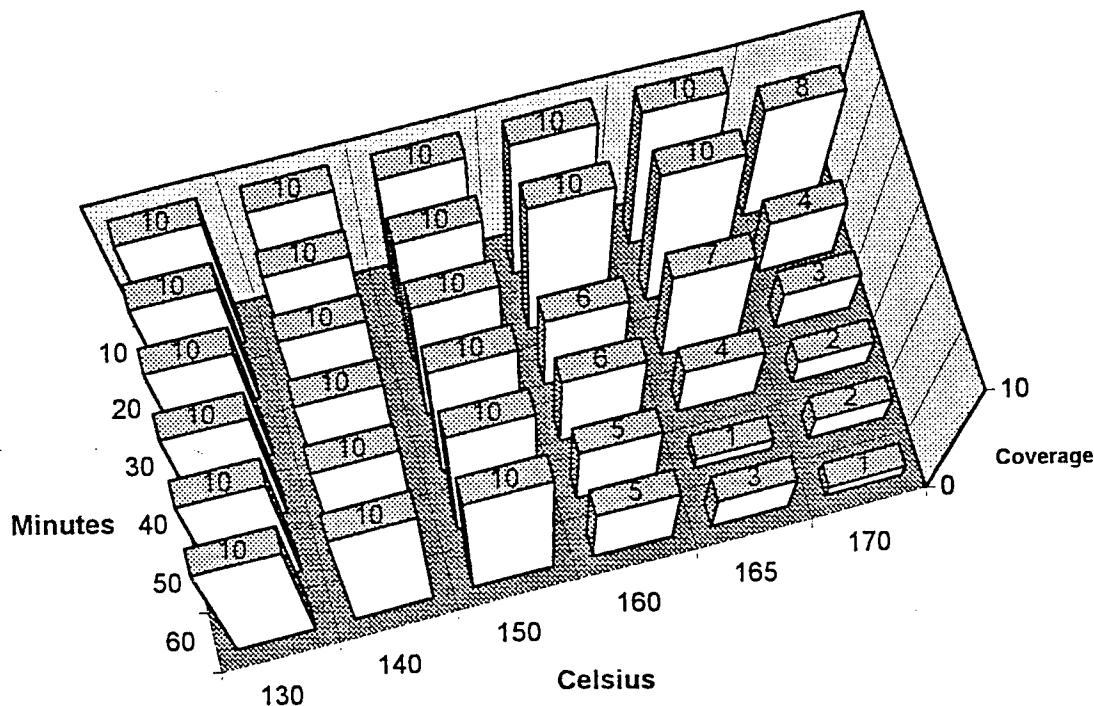


Figure 2 - Time-temperature-coverage graph for the powder painting of glass slides.

It was of interest to determine whether the transition from good to poor coating under certain drying conditions was due to the inability of the antistat to provide surface conductivity. This loss of surface conductivity could be the result of evaporation/sublimation of the antistat coating during drying. In order to relate the efficiency of electrostatic powder coating to the surface conductivity of glass slides treated with the antistat, surface resistivity measurements were made. In these tests, glass slides were initially coated with the antistat and the resistivity was measured after the antistat was air dried for 30 minutes at 29°C. Following the measurements, the slide were placed in an oven at 165°C. A series of tests were performed by varying drying time (20, 30 and 40 minutes). Surface resistivity data obtained from these tests are shown in Figure 3. It may be seen that the mean resistivity of antistat covered glass slides increased with increasing drying time. Figure 3 presents the surface resistivity of the glass slides before and after being placed into the oven. A statistical analysis (t-test) conducted on the "before" heat treatment data and the "after" heat treatment data, at a level of confidence of 99%, showed that the mean surface resistivity increased on heating .

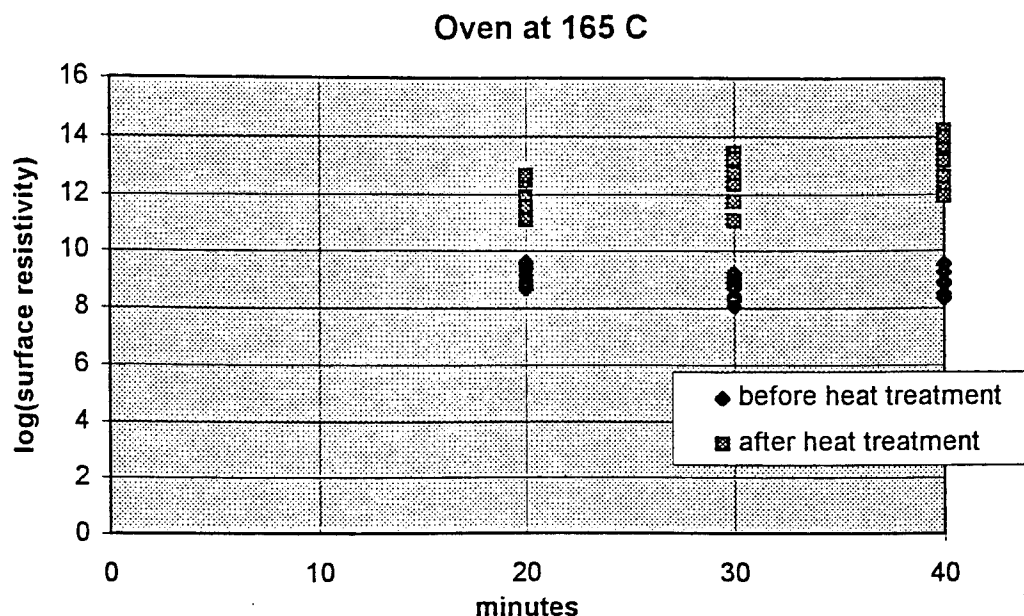


Figure 3 - Effect of heat treatment at 165°C on the surface resistivity of antistat covered glass slides.

There are two mechanisms by which an antistat may be inactivated by heating. The first mechanism is the removal of the solvent within the antistat that acts as a medium for charge transport. The second mechanism is the sublimation of the fatty quaternary ammonium salt. Thermogravimetric analysis was performed to characterize the weight loss of the antistatic coating at the epoxy powder curing temperature (171°C). The antistat was sprayed into an aluminum dish and was placed in an air-circulating oven at 120°F overnight in order to expel the hydrocarbons (in the propellant) from the antistat. After drying the sample in the oven, it was placed in the TGA chamber which was purged with dry air. The temperature was ramped at 100°C/min to 171°C and held at this temperature for 120 minutes. As shown in Figure 4, the antistat lost 22.3 wt% of its initial dried weight after 2 hours. The sublimation of the antistat offers the possibility to set the surface resistivity by controlled removal of deposited antistat.

TGA File Name: stat4
 Sample Weight: 18.358 mg
 Sat Sep 24 11:04:22 1994
 PERKIN-ELMER
 7 Series Thermal Analysis System
 Anti-Static Agent

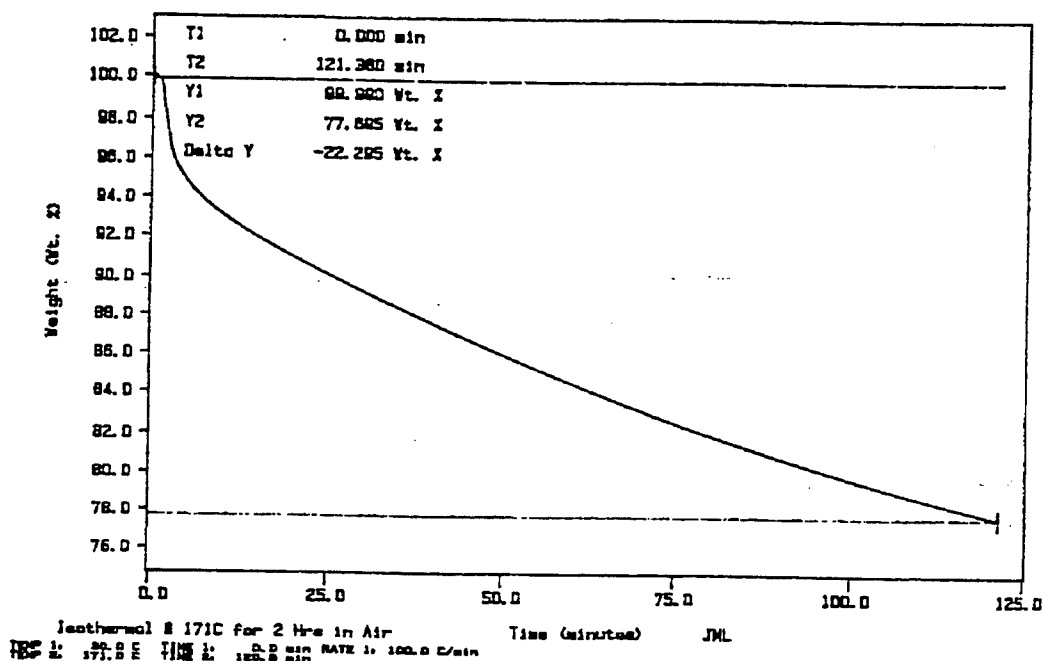


Figure 4 - Weight loss suffered by aerosol antistat at 171°C.

Thermogravimetric analysis was extended to higher temperature to find out whether the antistat material can be completely removed at higher temperatures. The aerosol antistat was first sprayed into the TGA pan, heated to 100°C and held for 30 minutes under dry nitrogen. At the end of this holding period the sample was cooled to 30°C. The sample was then ramped to 500°C at 10°C per minute. As shown in Figure 5, the antistatic coating lost over 90% of its dry weight between 187°C and 336°C. These results confirm the earlier premise that the antistat sublimates on heating.

TGA File Name: stat1
 Sample Weight: 3.450 mg
 Fri Jul 29 11:08:24 1994

PERKIN-ELMER
 7 Series Thermal Analysis System

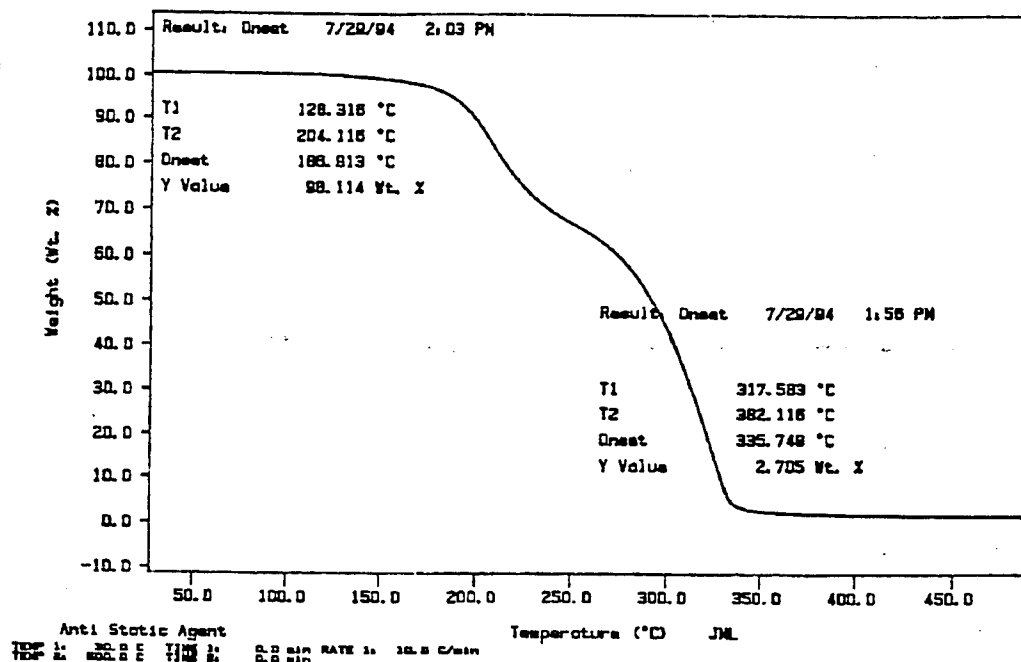


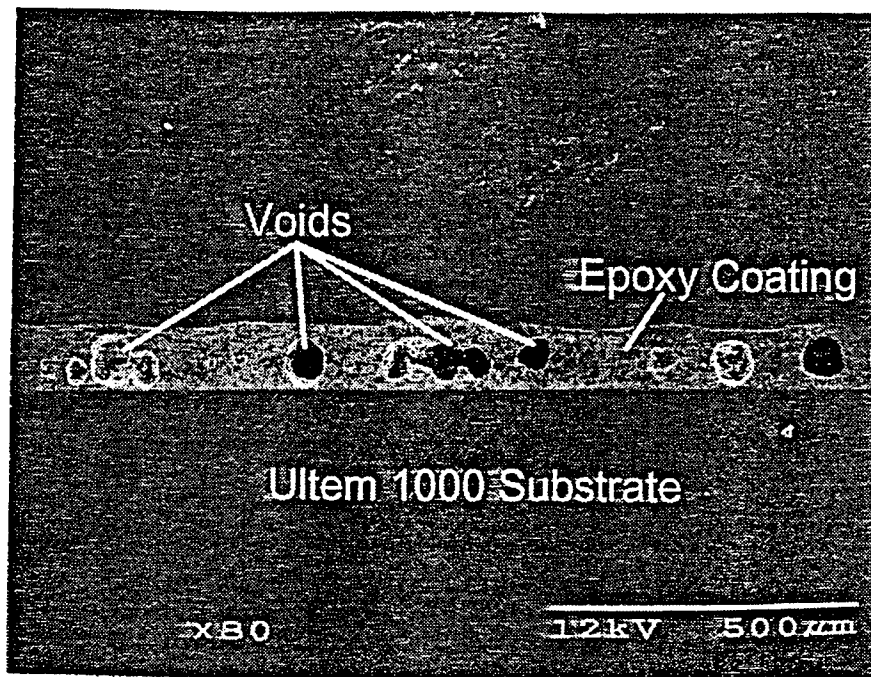
Figure 5 - Thermogravimetric Analysis of aerosol antistat.

The next step in the investigation was to test whether the epoxy coatings formed on antistat treated Ultem can pass military specifications. Epoxy coatings of thickness 64-89 μm formed on Ultem were subjected to adhesion and fluid resistance tests. As shown in Table II, the coatings passed the military specifications tests.

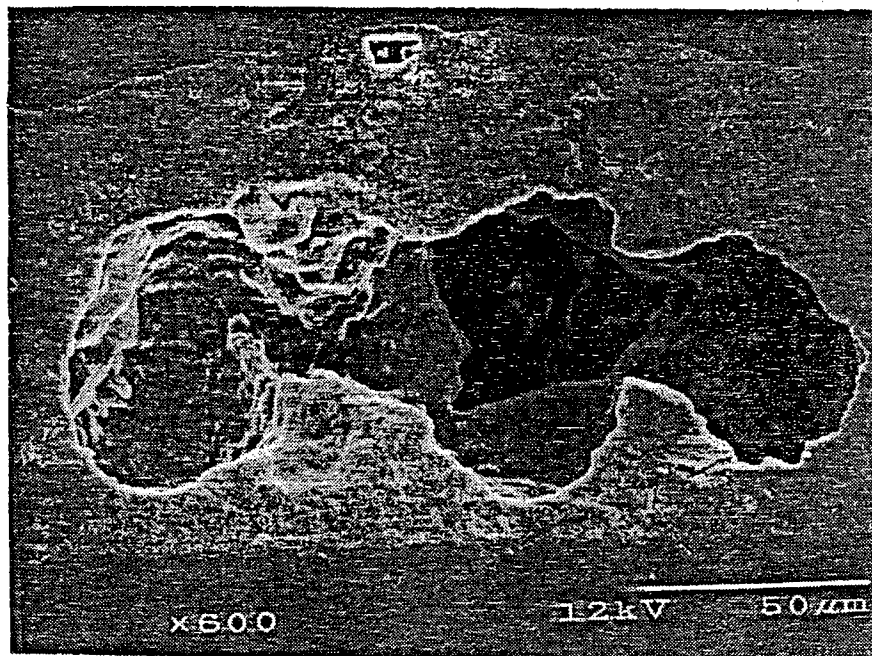
Table II Results of Physical Performance Tests

SUBSTRATE TYPE	WET TAPE ADHESION TEST	LUBRICATION OIL	HYDRAULIC FLUID	HYDROCARBON SOLVENT
Ultem substrate with aerosol antistat	5A	pass	pass	pass

The morphology and microstructure of the epoxy coatings were studied to see if the loss of antistat during the epoxy curing would cause any defects in the coating. An Ultem substrate was treated with an aerosol antistat and then powder painted and cured at 171°C for 35 minutes. After powder painting, the Ultem substrate was cut normal to its surface to expose the internal morphology and microstructure of the polymeric coating. As shown in Figures 6a and 6b, a vapor phase was trapped within the polymeric coating creating voids.



(a)



(b)

Figure 6 - SEM micrographs of polymeric coating on Ultem substrate: (a) Magnification 80X, and (b) Magnification 600X.

The void shown in Figure 6b is over 150 μm in length. An experiment was conducted to check if the voids were created from the out-gassing of the substrate during curing or from the antistat. A bare Ultem 1000 substrate was half covered with an aluminum tape, and placed into an oven at 171°C for 15 minutes. After being in the oven for 15 minutes, the substrate was dipped in the powder hopper and later cured. The cross section of the bare Ultem side covered with epoxy coating showed voids with diameters 50 μm or more. The cross section of the coating formed on the side with aluminum tape did not have these voids as shown in the sketch in Figure 7. The results of this experiment showed that something was evolving from the substrate and the aluminum tape acted as a barrier preventing large void formation within the epoxy coating.

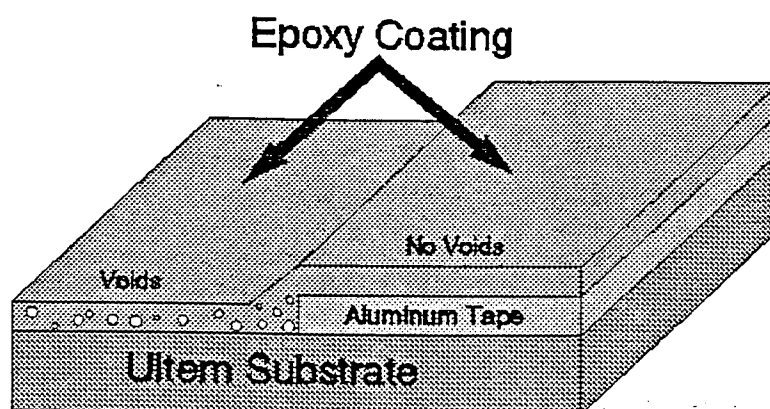
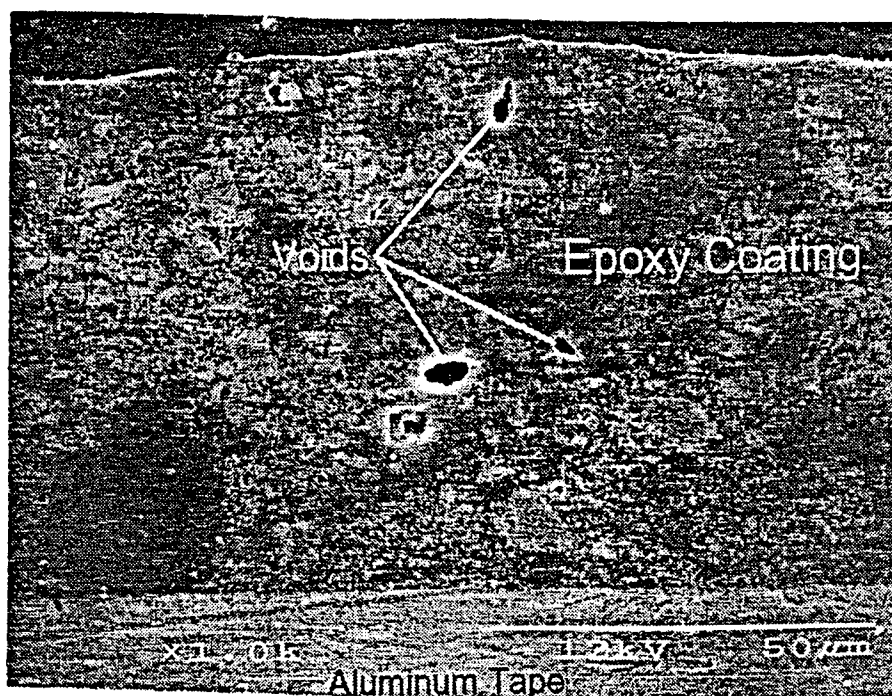
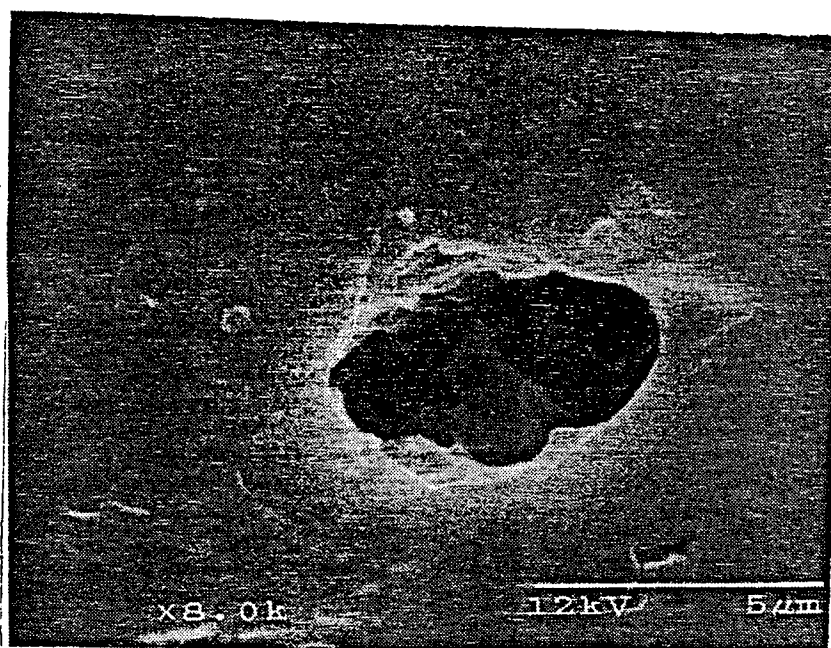


Figure 7 - Powder coating of a preheated (171°C) Ultem substrate half covered with aluminum tape.

Characterization of an epoxy coating formed on top of a antistat treated aluminum tape which covered an Ultem substrate was also carried out. The antistat was air dried at 29°C for 30 minutes prior to the coating step. From Figures 8a and 8b, it may be observed that the coating on aluminum also contained voids, but the void size as well as density was a lot lower than that observed in Figure 6a. From these results it may be concluded that the antistats also cause voids, but not to the extent caused by the polymeric substrate.



(a)



(b)

Figure 8a - SEM micrograph of aluminum tape treated with aerosol antistat and then powder painted and cured at 171°C for 35 minutes: (a) Magnification 1000X, and (b) Magnification 8000X.

If outgassing of the substrate were responsible for voids, then the density of voids could be reduced, if not eliminated, by substrate preheating. To test this, one set of PEEK and Ultem substrates was preheated to 165°C for 20 min. and then powder painted with the help of an antistat coating. The other set was powder painted without a preheating step. Figure 9 shows the total void densities (number of voids per unit area) determined from cross sectional areas at three different locations.

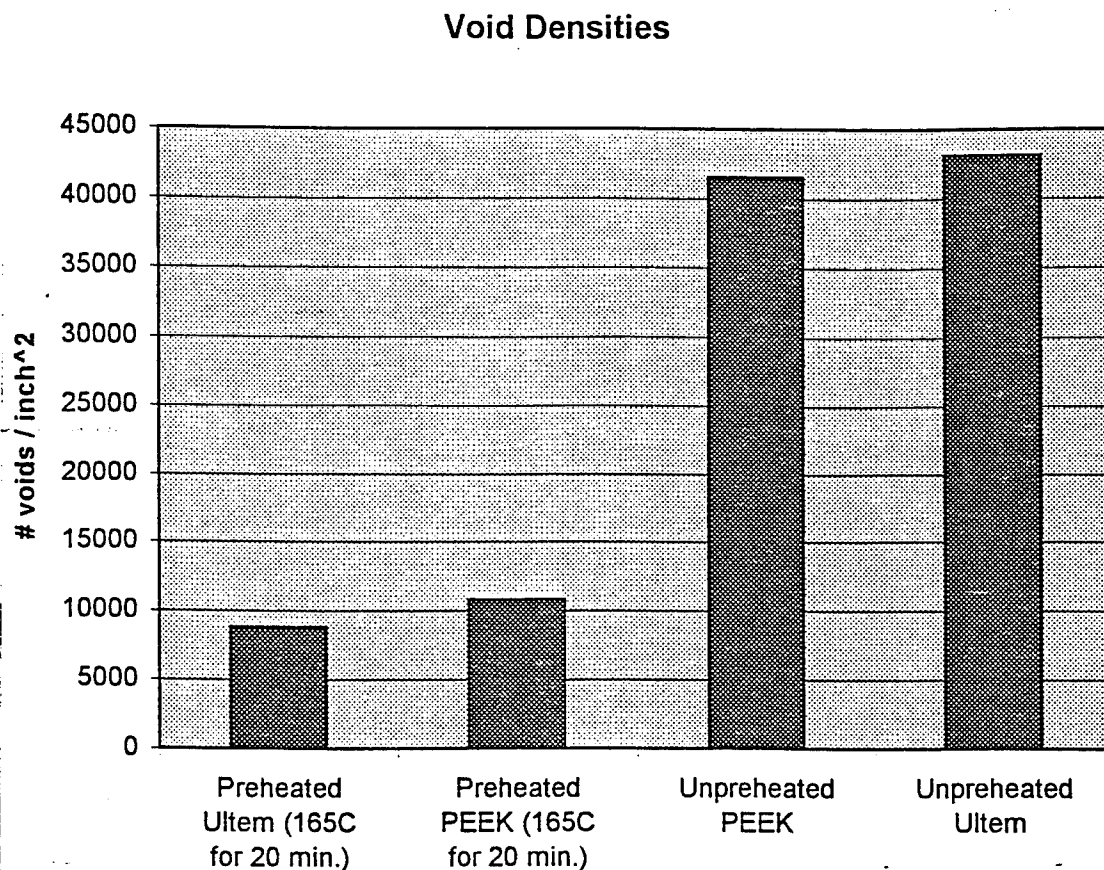


Figure 9 - The effect of substrate preheating on void densities.

The decrease in void density with preheating suggests that gases/vapors released from the substrate during the curing of the powder coatings are indeed trapped in the coating.

Thermogravimetric analysis was used to quantify the amount of volatile species evolving from the substrate during the curing of the epoxy coating. The Ultem substrate lost 0.32 wt% when ramping from 30°C to 171°C at 10°C per minute and held at 171°C for 35 minutes. Using GC/MS, the volatile species was identified to be water vapor (Figure 10). The nitrogen peak in the spectrum is due to the carrier gas used in the experiments. It is thus evident that substrate preheating prior to powder painting is an important step to prevent volatile from substrate from being trapped in the cured powder paint.

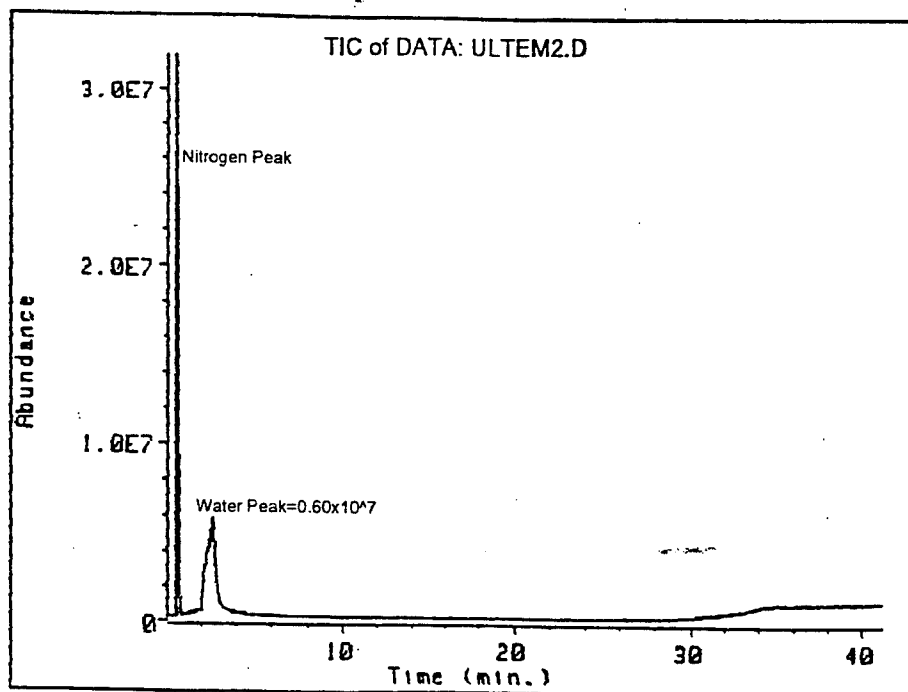


Figure 10 - GC/MS graph of Ultem 1000 where the vial was purged of air or ambient moisture by nitrogen gas prior to heating the vial.

Conclusions

An effective method to electrostatically powder coat non-conductive substrate has been developed. This involves the use of an aerosol antistat containing a quaternary ammonium compound. The efficiency of powder coating is related to the surface resistivity of the sample which can be controlled by the application of the antistatic coating. While the epoxy coating on an antistat treated non-conductive substrate passed the adhesion and solvent resistance test, microstructure analysis showed that there are voids in the epoxy coating. It appears that the water content of the substrate is responsible in creating these large voids (50 μm in diameter or larger) within the epoxy coating.

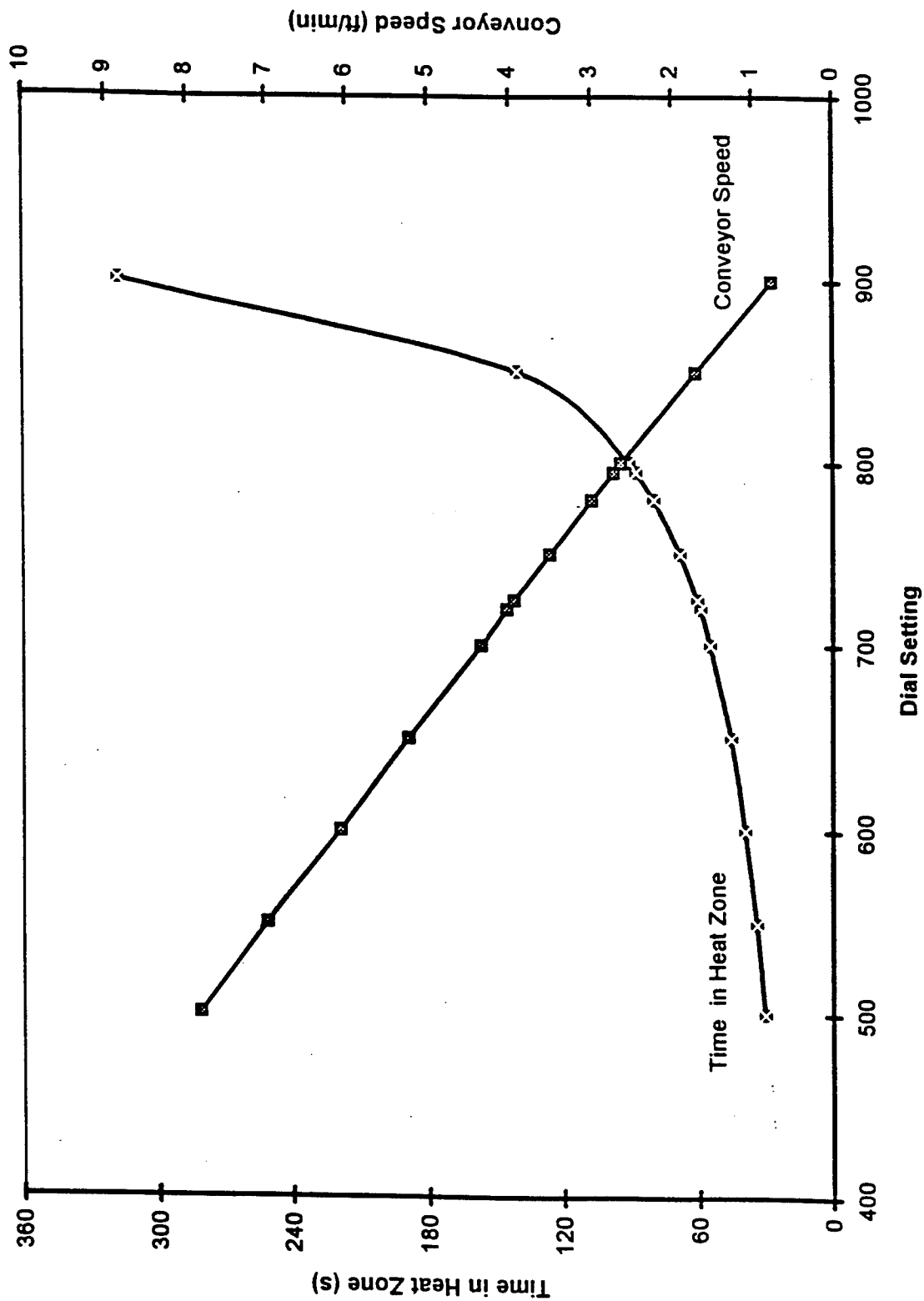
References

1. Hughes Missile Systems Group, "Industrial Modernization Incentives Program Final Technical Report", Contract No. F08635-85-C-0079, (1991)
2. A.A. Elmoursi and D.P. Garner, "Electrostatic Painting of Plastics II: Electric Field Effects", Journal of Coatings Technology, 64 (805) (1992), 39-44.
3. H. Fujiwara, K. Motogami and K. Mori, "Method for Electrostatic Coating of a Resin Molding," U.S. Patent #5,137,748.
4. B. Davis, "Antistatic/Conductivity Additives in Paint and Plastics", Industrial Applications of Surfactants, 59 (1986) 307-317.

APPENDIX C

IR Cure Profile Results

IR Oven Conveyor Calibration



UNCLASSIFIED

PAINTED PANEL TESTING



HUGHES MISSILE SYSTEMS COMPANY

RESULTS

<u>Oven Dwell (s)</u>	<u>Hold Time (s)</u>	<u>Peak Temperature (°F)</u>	<u>Solvent Resistance</u>
30	0	415	poor
90	0	411 - 425	fair (loss of gloss)
-	90	410	good
	180	425	good but yellowing

APPENDIX D

Powder Coating Development Test Results

Approved for public release; distribution is unlimited.

Approved for public release; distribution is unlimited.

EVALUATION OF: Herberts Powder Coati Date: 13 JAN 95

Substrate: Al and steel

Pretreatment: varied

TABLE II

		070-70-1	073-63-2	073-63-3	089-18-1	089-18-2	073-72-4
ADHESION:							
Dry Tape "A" Method	std	5A	5A	4A	5A	5A	5A
Wet Tape (24 hr / RT)	std	5A	5A	5A	5A	5A	5A
Wet Tape (4 day / 120°F)	std	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	std	5A	5A	4A	5A	5A	5A
Dry Tape "A" Method	St-BG	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	St-BG	0A	1A	0A	2A	1A	1A
Dry Tape "A" Method	St-ZPG	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	St-ZPG	4A	5A	2A	4A	4A	5A
FLUID/CORROSION RESISTANCE:							
Salt Spray (2000 hr)	std	P	P	P			
Salt Spray (500 hr)	St-BG	F	+ (1)	P	F	-	-
Salt Spray (500 hr)	St-ZPG	P	P (1)	P	+	+	+
SO2 Spray (500 hr)	std	-	-	-	-	-	-/F
SO2 Spray (96 hr)	St-BG	F	F (1)	P	F	-	-
SO2 Spray (96 hr)	St-ZPG	P	P (1)	P	P	P	P
H2O Resistance (24 h/RT)		P	P	P	P	P	P
H2O Resistance (4 d/120°F)		P	P	P	P	P	P
H2O Resistance (7 d/150°F)		P	P	P	P	P	P
Humidity Resistance	std	P	P	P	P	P	P
23699 Oil (24 hr / 250°F)	std						
83282 Hydraulic(24 h/150°F)	std						
Hydrocarbon JP-5(7d/RT)	std						
Solvent Resistance	std	P	P	P	P	P	P
Filiform Corrosion	alclad	P	P/B	B/F			
EIS	std						
FLEXIBILITY:							
GE Impact test)	flex	10/5	2	2	0.5	0.5	0.5
Mandrel Bend (-60°F)	flex	0.25	>0.25	>0.5	0.125	>0.5	>0.5
MISCELLANEOUS:							
Gloss (60°)		88.7	90.6	96.2	65.4	73.2	90.1
Retain	std						

Note: std = 2024 T3 with CCC, alclad = 2024 T3 Alclad with CCC, flex = 2024 T0 with CAA

St-BG = 1010 Steel Bare Ground On One Side, St-ZPG = 1010 Steel with Zinc Phosphate Pretreatm

Single diagonal scribe for corrosion test on steel substrates.

Substrate: Al and steel

Pretreatment: varied

TABLE II Cont

		255-89-1	255-89-2	255-89-3	255-89-4	255-90-1	255-90-2	255-90-3
ADHESION:								
Dry Tape "A" Method	std	5A	5A	5A	5A	5A	5A	5A
Wet Tape (24 hr / RT)	std	5A	5A	5A	5A	5A	5A	5A
Wet Tape (4 day / 120°F)	std	5A	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	std	5A	5A	5A	5A	5A	5A	5A
Dry Tape "A" Method	St-BG	5A	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	St-BG	0A	1A	1A	1A	0A	0A	1A
Dry Tape "A" Method	St-ZPG	5A	5A	5A	4A	5A	5A	5A
Wet Tape (7 day / 150°F)	St-ZPG	5A	4A	5A	3A	5A	4A	5A
FLUID/CORROSION RESISTANCE:								
Salt Spray (2000 hr)	std							
Salt Spray (500 hr)	St-BG	+/-	P/+	-	F	+ (1)	F	-
Salt Spray (500 hr)	St-ZPG	+	P/+	+	+	+	+	P/+
SO2 Spray (500 hr)	std	-	P/+	P	-	-	+	+
SO2 Spray (96 hr)	St-BG	P	P/+	P	-	P (1)	-	P
SO2 Spray (96 hr)	St-ZPG	P	P	P	+	P	P	P
H2O Resistance (24 h/RT)		P	P	P	P	P	P	P
H2O Resistance (4 d/120°F)		P	P	P	P	P	P	P
H2O Resistance (7 d/150°F)		P	P	P	P	P	P	P
Humidity Resistance	std	P	P	P	P	P	P	P
23699 Oil (24 hr / 250°F)	std							
83282 Hydraulic(24 h/150°F)	std							
Hydrocarbon JP-5(7d/RT)	std							
Solvent Resistance	std	P	P	P	P	P	P	P
Filiform Corrosion	alclad							
EIS	std							
FLEXIBILITY:								
GE Impact test)	flex	20	2	5	5	40	20	10
Mandel Bend (-60°F)	flex	>0.25	>0.25	>0.25	>0.5	>0.25	0.125	>0.25
MISCELLANEOUS:								
Gloss (60°)		79.8	82.7	55.3	58.8	100.8	92.1	94.4
Retain	std							

Note: std = 2024 T3 with CCC, alclad = 2024 T3 Alcad with CCC, flex = 2024 T0 with CAA

St-BG = 1010 Steel Bare Ground On One Side, St-ZPG = 1010 Steel with Zinc Phosphate Pretreatment Ground O

Single diagonal scribe for corrosion test on steel substrates.

EVALUATION OF: Morton Powder Coatings

Date: 13 JAN 95

Substrate: Al and steel

Pretreatment: varied

TABLE II cont

ADHESION:		255-92-1	255-92-2	255-92-3	255-95-1	255-95-2	255-95-3
Dry Tape "A" Method	std	5A	4A	5A	5A	5A	5A
Wet Tape (24 hr / RT)	std	5A	5A	5A	4A	5A	5A
Wet Tape (4 day / 120°F)	std	5A	5A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	std	5A	5A	5A	4A	5A	5A
Dry Tape "A" Method	St-BG	5A	4A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	St-BG	1A	3A	5A	1A	0A	3A
Dry Tape "A" Method	St-ZPG	5A	4A	5A	5A	5A	5A
Wet Tape (7 day / 150°F)	St-ZPG	5A	3A	5A	3A	4A	5A
FLUID/CORROSION RESISTANCE:							
Salt Spray (2000 hr)	std						
Salt Spray (500 hr)	St-BG	F	F	F	-	-	F
Salt Spray (500 hr)	St-ZPG	F	-	F	-	+	+
SO2 Spray (500 hr)	std	F	P	P/+	+/-	P/+	P/+
SO2 Spray (96 hr)	St-BG	P	F	F	P	-	P
SO2 Spray (96 hr)	St-ZPG	P	P	F	P	P	P
H2O Resistance (24 h/RT)		P	P	P	P	P	P
H2O Resistance (4 d/120°F)		P	P	P	P	P	P
H2O Resistance (7 d/150°F)		P	P	P	P	P	P
Humidity Resistance	std	P	P	P	P	P	P
23699 Oil (24 hr / 250°F)	std						
83282 Hydraulic (24 h/150°F)	std						
Hydrocarbon JP-5 (7d/RT)	std						
Solvent Resistance	std	P	P	F@45	P	P	P
Filiform Corrosion	alclad						
EIS	std						
FLEXIBILITY:							
GE Impact test	flex	1	1	2	20	2	1
Mandrel Bend (-60°F)	flex	0.25	>0.25	0.25	>0.5	>0.25	>0.25
MISCELLANEOUS:							
Gloss (60°)		1.1	2.0	0.6	95.3	88.2	84.7
Retain	std						

Note: std = 2024 T3 with CCC, alclad = 2024 T3 Alclad with CCC, flex = 2024 T0 with CAA

St-BG = 1010 Steel Bare Ground On One Side, St-ZPG = 1010 Steel with Zinc Phosphate Pretreatment Ground On One Side

Single diagonal scribe for corrosion test on steel substrates.

TABLE III

	M003	M005	M006	M007	M008	M009	M010	M011	M012	M013
Cure Temperature, F	300	300	300	300	300	300	300	300	300	300
Cure Time, Min.	30	30	30	30	30	30	30	30	30	30
Material Type	Hard Epoxy	Acrylic	Epoxy	Epoxy/Phnlic	Epoxy/Phnlic	Hybrid	Hard Epoxy	Epoxy	Epoxy	Acrylic
Color	Grey	Grey	Grey	Grey	Grey	Grey	Grey	Grey	Grey	Grey
Tape Test, 24 Hr. Water Soak	5A	5A	5A	5A	5A	5A	3A	5A	5A	5A
Tape Test, 96 Hr. Water Soak	5A	5A	5A	5A	5A	5A	3A	5A	5A	5A
Tape Test, 168 Hr. Water Soak	4A	5A	4A	5A	5A	5A	3A	5A	5A	5A
JP4 Fluid Resistance	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Lubricating Fluid	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Hydraulic Fluid	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Salt Fog, 500 Hr.	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Salt Fog, 2000 Hr.	(NO TEST)	4/4 PASS	4/4 PASS	4/4 PASS	4/4 PASS	4/4 PASS	3/4 FAIL	4/4 PASS	3/4 PASS	4/4 FAIL
SO2/Salt Fog, 500 Hour	(NO TEST)	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING
EIS	(NO TEST)	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING
Flexibility, 42 Inch, %	>60 PASS	20	>60 PASS	>60 PASS	>60 PASS	>60 PASS	>60 PASS	>60 PASS	>60 PASS	>60 PASS
Cure Temperature, F	250	275	300	300	300	250	250	250	250	250
Cure Time, Min.	35	35	35	35	35	30	30	30	30	30
Material Type	Epoxy	Acrylic	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy	Epoxy
Color	White	White	White	White	White	Clear	Clear	Clear	Clear	Clear
Tape Test, 24 Hr. Water Soak	3A	3A	5A	5A	5A	5A	3A	5A	3A	3A
Tape Test, 96 Hr. Water Soak	3A	3A	5A	4A	4A	5A	4A	5A	4A	4A
Tape Test, 168 Hr. Water Soak	3A	3A	4A	3A	3A	5A	3A	5A	3A	3A
JP4 Fluid Resistance	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Lubricating Fluid	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Hydraulic Fluid	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS	PASS
Salt Fog, 500 Hr.	MARGINAL	PASS	PASS	PASS	PASS	(NO TEST)	PASS	(NO TEST)	PASS	PASS
Salt Fog, 2000 Hr.	3/4 PASS	4/4 PASS	4/4 PASS	3/4 PASS	3/4 PASS	4/4 FAIL	4/4 PASS	2/4 PASS	4/4 PASS	4/4 PASS
SO2/Salt Fog, 500 Hour	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING	---	PENDING	---	---
EIS	PENDING	PENDING	PENDING	PENDING	PENDING	PENDING	---	PENDING	---	---
Flexibility, 42 Inch, %	>60 PASS	10	>40/<60	>60 PASS	>60 PASS	5	---	20	---	---

Hughes Missile Systems Company
Components and Materials Engineering Department
Materials and Processes Analysis Laboratory

Rev 1.3(DRM) 95.01.17
Page 1 of 1

3A or below is low - 10 days

Approved for public release; distribution is unlimited.

Results Comparison

HMSC, NAWC
TABLE IV

	Herberts		Herberts	
	073-63-2		070-70-1	
	HMSC	NAWC	HMSC	NAWC
Material	Epoxy	Epoxy	Epoxy	Epoxy
Inhibitor	Z14L	Z14L	Z14L/TIO	Z14L/TIO
PVC	25	25	30 (25/5)	30 (25/5)
Color	Clear/Haze	Clear/Haze		
Cure Temp	250	250	250	250
Cure Time	35	30	35	30
Adhesion, Wet Tape, 24 Hr., Al	5A	5A	5A	5A
Adhesion, Wet Tape, 96 Hr., Al	5A	5A	5A	5A
Adhesion, Wet Tape, 168 Hr., Al	5A	5A	5A	5A
Adhesion, Wet Tape, 24 Hr., Steel	3A		3A	
Adhesion, Wet Tape, 96 Hr., Steel	4A		4A	
Adhesion, Wet Tape, 168 Hr., Steel	3A	5A	3A	4A
Salt Spray, 500 Hr., Al				
Salt Spray, 2000 Hr., Al	4/4 FAIL	PASS	2/4 FAIL	PASS
Salt Spray, 500 Hr., Steel	PASS	PASS (1)	PASS	PASS (1)
Salt Spray, 2000 Hr., Steel	4/4 PASS		4/4 PASS	
SO2/Salt Spray, 500 Hr., Al				
SO2/Salt Spray, 96 Hr., Steel		PASS (1)		PASS
Water Resistance, 24 Hr., RT		PASS		PASS
Water Resistance, 96 Hr., 120F		PASS		PASS
Water Resistance, 168 Hr., 150 F		PASS		PASS
JP4 Resistance	PASS		PASS	
Lubricating Fluid Resistance	PASS		PASS	
Hydraulic Fluid Resistance	PASS		PASS	
Solvent Resistance		PASS		PASS
Filiform Corrosion		P/B		P
Impact, GE 42 Inch	5	2	20	10/5
Gloss		90.6		88.7

TABLE V

Evaluation of either a primer & topcoat system or a self-priming topcoat (SPT)
based on data from a single substrate

Name and file number of coating: M255892Z

Date: 16 JAN 95

Description: MORTON POWDER COATING (ZDOC)

Weight Factor:	Test Name:	Substrate:	Range:	Lab Data:	Notes:
0.0	Dry Scrape		0.5 - 10+ kg		
0.0	Wet Scrape (7d/ 150°F)		0.5 - 10+ kg		
4.8	Dry Tape "A" method	S	0 - 5 (A)	5.0	Excellent
0.0	Wet Tape (24 hr/ RT)		0 - 5 (A)		
0.0	Wet Tape (4d/ 120°F)		0 - 5 (A)		
9.8	Wet Tape (7d/ 150°F)	S	0 - 5 (A)	4.0	Satisfactory

Fluid/ Corrosion Resistance:		(100 = P), (66 = +), (33 = -), (0 = F)			Notes:
Weight Factor:	Test Name:	Substrate:	Range:	Lab Data:	
9.8	Salt Spray (500 hr)	S	0 - 100	83.0	Satisfactory
0.0	Salt Spray (D 1654) Scribe		% Area		
0.0	Salt Spray (D 1654) Gen Surf		0 - 10		
8.2	SO2 Spray (96 hr)	S	0 - 100	100.0	Excellent
0.0	SO2 Spray (D 1654) Scribe		% Area		
0.0	SO2 Spray (D 1654) Gen Surf		0 - 10		
0.0	H2O resistance (24 hr/ RT)		0 - 100		
0.0	H2O resistance (4 d/ 120°F)		0 - 100		
9.0	H2O resistance (7 d/ 150°F)	A	0 - 100	100.0	Excellent
0.0	Humidity Resistance		0 - 100		
0.0	23699 Oil (24 hr/ 250°F)		0 - 100		
0.0	83282 Hydraulic (24 hr/ 150°F)		0 - 100		
0.0	Hydrocarbon JP-5 (7 d/ RT)		0 - 100		
0.0	Solvent Resistance		0 - 100		
0.0	Heat Resistance (4 hr/ 250°F)		0 - 100		
0.0	Filiform Corrosion		0 - 100		

Flexibility:					Notes:
Weight Factor:	Test Name:	Substrate:	Range:	Lab Data:	
0.0	GE Impact test (gloss)		0.5%-60%		
0.0	GE Impact test (camouflage)		0.5%-60%		
0.0	Mandrel bend (-60°F)		0.125"...0.75"		

Miscellaneous:		Put "x" in substrate box below if using wt factors for misc tests			Notes:
Weight Factor:	Test Name:	Substrate:	Range:	Lab Data:	
0.0	Admix Viscos (Ford #4)		seconds		
0.0	2 Hr Pot Life (Ford #4)		seconds		
0.0	4 Hr Pot Life (Ford #4)		seconds		
0.0	Set-To-Touch		hours		
0.0	Dry Hard		hours		
0.0	60° Gloss (gloss)		unitless		
0.0	60° Gloss (camouflage)		unitless		
0.0	85° Gloss (camouflage)		unitless		
0.0	Color Match (delta E)		unitless		

NOTES:

Overall Rating: 88.2

48

TABLE V CONT

Evaluation of either a primer & topcoat system or a self-priming topcoat (SPT)
based on data from a single substrate

Name and file number of coating: H070701A

Date: 16 JAN 95

Description: HERBERTS POWDER COATING (ZDOC)

Weight Factor:	Test Name:	Substrate:	Range:	Lab Data:	Notes:
0.0	Dry Scrape		0.5 - 10+ kg		
0.0	Wet Scrape (7d/ 150°F)		0.5 - 10+ kg		
4.6	Dry Tape "A" method	A	0 - 5 (A)	5.0	Excellent
10.0	Wet Tape (24 hr/ RT)	A	0 - 5 (A)	5.0	Excellent
10.0	Wet Tape (4d/ 120°F)	A	0 - 5 (A)	5.0	Excellent
10.0	Wet Tape (7d/ 150°F)	A	0 - 5 (A)	5.0	Excellent

Fluid/ Corrosion Resistance:		(100 = P), (66 = +), (33 = -), (0 = F)			
0.0	Salt Spray (2000 hr)		0 - 100		
0.0	Salt Spray (D 1654) Scribe		% Area		
0.0	Salt Spray (D 1654) Gen Surf		0 - 10		
8.8	SO2 Spray (500 hr)	A	0 - 100	33.0	Borderline Failure
0.0	SO2 Spray (D 1654) Scribe		% Area		
0.0	SO2 Spray (D 1654) Gen Surf		0 - 10		
9.0	H2O resistance (24 hr/ RT)	A	0 - 100	100.0	Excellent
9.0	H2O resistance (4 d/ 120°F)	A	0 - 100	100.0	Excellent
9.0	H2O resistance (7 d/ 150°F)	A	0 - 100	100.0	Excellent
7.0	Humidity Resistance	A	0 - 100	100.0	Excellent
0.0	23699 Oil (24 hr/ 250°F)		0 - 100		
0.0	83282 Hydraulic (24 hr/ 150°F)		0 - 100		
0.0	Hydrocarbon JP-5 (7 d/ RT)		0 - 100		
5.4	Solvent Resistance	A	0 - 100	100.0	Excellent
0.0	Heat Resistance (4 hr/ 250°F)		0 - 100		
0.0	Filiform Corrosion		0 - 100		

Flexibility:					
9.0	GE Impact test (gloss)	A	0.5%-60%	7.5	Borderline Failure
0.0	GE Impact test (camouflage)		0.5%-60%		
0.0	Mandrel bend (-60°F)		0.125"...0.75"		

Miscellaneous:		Put "x" in substrate box below if using wt factors for misc tests			
0.0	Admix Viscos (Ford #4)		seconds		
0.0	2 Hr Pot Life (Ford #4)		seconds		
0.0	4 Hr Pot Life (Ford #4)		seconds		
0.0	Set-To-Touch		hours		
0.0	Dry Hard		hours		
0.0	60° Gloss (gloss)		unitless		
0.0	60° Gloss (camouflage)		unitless		
0.0	85° Gloss (camouflage)		unitless		
0.0	Color Match (delta E)		unitless		

NOTES:

Overall Rating: 86.4

TABLE VI

TOTAL PERFORMANCE EVALUATION (TPE) COMPARISON

	H	H	H	H	H	H	H	M	M	M	M	M	M	M	M	M	M	M	M	M
	0	0	0	0	0	0	0	2	2	2	2	2	2	2	2	2	2	2	2	2
	7	7	7	8	8	7	7	5	5	5	5	5	5	5	5	5	5	5	5	5
	0	3	3	9	9	3	3	5	5	5	5	5	5	5	5	5	5	5	5	5
	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	7	6	6	1	1	7	8	8	8	8	9	9	9	9	9	9	9	9	9	9
	0	3	3	8	8	2	9	9	9	9	0	0	0	2	2	2	5	5	5	5
	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	1	2	3	1	2	4	1	1	2	3	4	1	2	3	1	2	3	1	2	3
AI	86.4	84.5	79.7	84.5	84.5	82.5	90.3	89.3	93.1	86.4	92.3	94.2	92.2	82.5	89.7	84.0	83.8	89.3	89.3	89.3
ZP Steel	92.9	100	78.8	85.9	85.9	92.9	92.9	88.2	92.9	67.1	92.9	85.9	95.3	78.8	63.6	61.1	67.0	85.9	92.9	92.9
AVG	87.55	92.25	79.25	85.2	85.2	87.7	91.6	88.75	93.0	76.75	92.6	90.05	93.75	80.65	76.65	72.55	75.4	87.6	91.1	91.1